

THE POLAROGRAPHIC STUDIES ON TERNARY COMPLEXES OF SOME TRANSITION METAL IONS WITH BIOLOGICALLY IMPORTANT LIGANDS

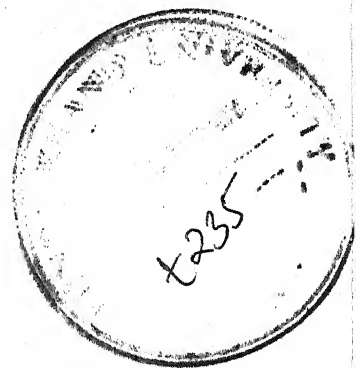
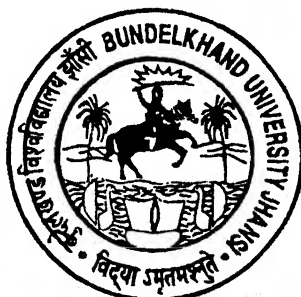
THESIS

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By

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Last but not the least, I take this opportunity to record my thanks to all persons who worked with me and also who have been directly or indirectly helpful to me.

Place : ORAI


(**UDAI PRATAP SINGH**)

Dated : 19.7.2002 Dayanand Vedic Postgraduate College, Orai

CERTIFICATE

This is to certify that Shri Udai Pratap Singh, M.Sc., a candidate for the degree of Doctor of Philosophy in Chemistry of Bundelkhand University, Jhansi, has worked under my guidance on, "The Polarographic studies on ternary complexes of some transition metal ions with biologically important ligands."

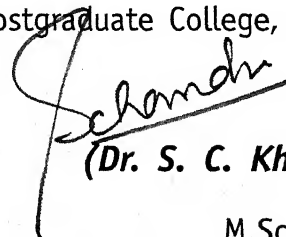
It is my firm opinion that he has taken enough pains to make the thesis upto the standard both in respect of contents and literary presentation.

I further certify that to the best of my knowledge, the work and approach is entirely original and it has not been carried out in the same manner or form anywhere else.

Shri Singh has put in more than two hundred days of work in the chemical laboratory of Dayanand Vedic Postgraduate College, Orai.

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CHAPTER - I

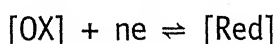
POLAROGRAPHY

Introduction and Developments

1.01 INTRODUCTION :

J. Heyrovsky¹ discovered polarography as a tool of analysis in which current is measured as a function of applied potential using a Dropping Mercury Electrode (DME). This technique is now widely used in physicochemical investigations. Significant among these applications is the study of kinetics of rapid reactions by Bridicka and co-workers.² Delahay³ and Kuta⁴ have reported the application of the tool in the study irreversible electrode processes.

In the method of polarography, an electroreducible or electrooxidisable species is allowed to reduce/oxidise in a cell consisting of a DME and some reference electrode. (Fig. 1.01). As the potential applied between them is varied, current flowing through electrode changes which is noted by means of a sensitive galvanometer. The DME functions as a cathode when there is reduction taking place in its vicinity and as an anode when oxidation occurs. For a reversible such reaction, the general expression may be written as follows.



Where [OX] represents the oxidant, [Red] the reductant, e an electron and n the number of electrons involved in the reaction.

When a stirred solution containing a reducible/oxidisable species is electrolysed between two large inert electrodes, the current voltage curve assumes a form shown in (Figure 1.02). If the applied potential is less than the decomposition potential, a small current flows through the circuit. As the potential is raised, the current is governed by Ohm's law i.e.

$$i = E - E_d/R$$

where i is the current flowing through the circuit, R is the resistance to the current, whereas E and E_d stand for applied potential and the decomposition potential respectively of the electroactive species. In such a scenario, the concentration of the electroactive species at electrode and in the bulk of the solution remains equal and their concentration polarisation can not occur. But, on the other hand, if the cathode is a microelectrode and the solution is unstirred, the electrolysis will lead to a shape of current voltage curve as shown in (Figure 1.03). As the applied voltage is increased, the concentration of the electroactive species decreases at the surface of the electrode until it becomes virtually zero. Any further increase in potential does not result in increase in current as the rate of reduction/oxidation of the electroactive species is now equal to the rate at which it reaches microelectrode. We say that the micro electrode is concentration polarised and the resulting current voltage curve is S - shaped which is called a polarogram, or a polarographic wave. The electroactive species is also called the depolariser.

The electroactive species can reach the surface of the electrode in two ways - by diffusion as well as by electrostatic attraction.

The current due to diffusion depends upon the difference in concentration of the depolariser ions in the bulk of the solution and the surface of the electrode.

On gradually increasing the applied potential beyond the decomposition potential the current increases but the concentration of the depolariser at the electrode surface decreases resulting in increase in the rate of diffusion transfer. A state is reached when depolariser is decomposed

at the electrode as rapidly as it reaches the microelectrode. Its concentration at the electrode surface is then considered to be zero for all practical purposes. Now the current due to diffusion remains constant on increasing the potential. Concentration polarization is said to have taken place. The final current is called the limiting current (i_l) and is composed of the initial current called the residual current (i_r), the migration current (i_m) and the diffusion current (i_d)

$$i_l = i_r + i_d + i_m$$

Among them, residual current itself consists of current flowing due to reduction of available impurities in electrolyte and condenser current or the non faradaic current. The condenser current is attributed to the continual charging of the new mercury drops of the DME due to the applied potential. The magnitude of residual current is usually very small. It is subtracted from the limiting current for all computational purposes. The existence of migration current may be attributed to the reduction of species that reaches the electrode exclusively through electrostatic attraction. It is the usual practice to minimise the migration current by adding high concentration of an indifferent electrolyte. The ions of the electrolyte are neither reduced nor oxidised in the range of potential applied and possess a high transport number. When this is done, the depolariser ions reaching electrode are controlled by diffusion alone and the current is called diffusion current (i_d).

The potential corresponding to half the diffusion current is called the half wave potential ($E_{1/2}$). The half wave potential is a characteristic property of the reducible/oxidisable species under given conditions. The

diffusion current is proportional to the concentration of electroactive species. Ilcovic⁵ derived an equation to express his proportionality. It may be written as

$$i_d = 706 n C D^{1/2} m^{2/3} t^{1/6}$$

for instantaneous current where the notations have their usual significance. The equation stands modified as follows for mean diffusion current

$$i_d = 607 n C D^{1/2} m^{2/3} t^{1/6}$$

If and when chemical equilibrium is set up at the micro-electrode the reduction/oxidation process is assumed to be reversible. On the other hand, if electrochemical reaction is slower so that electrochemical equilibrium is not attained, the process becomes irreversible.⁶⁻⁸

1.02 POLAROGRAPHY IN THE STUDY OF COMPLEX IONS IN SOLUTION

Polarography has emerged as powerful and versatile tool for the study of complex ions in solution. When a metal ion forms a complex, its diffusion current decreases due to formation of bulkier diffusing species and half wave potential exhibits a cathodic shift due to requirement of additional energy to first dissociate the complex species for the metal ion to reduce. These observations have been fruitfully utilized to establish methods for determining the composition and stability constants of single complexes by Lingane⁹ and those of successively formed complexes by DeFord and Hume¹⁰ provided the reduction is reversible and entirely diffusion controlled.

1.02.01 STUDIES ON SIMPLE COMPLEXES

A large number of investigators¹¹⁻²⁸ have polarographically studied complexes of a simple nature which undergo reversible, quasi reversible or irreversible reduction at the dropping mercury electrode.

When a system under goes quasi reversible or irreversible reduction, the reversible half wave potential, $E_{1/2}$, is determined by Gellings method²⁹ or by that of Hale and Parson³⁰. Thereafter the composition and stability constants of single or multiple complexes are easily determinable by Lingane⁹ or DeFord and Hume¹⁰ method as the case may be. For a change, some investigators³¹⁻³³ have applied the methods of Ringbom and Eriksson³⁴, Schwarzenbach³⁵⁻³⁷, Matsuda and Ayabe³⁸ and Crow^{39,40} and Tamamushi and Tanaka⁴¹ for the purpose of studying irreversibly reducible complexes.

Survey of literatures reveals that the studies on simple of complexes of Cd (II), Cu (II) and Pb (II) with ethylenediamine and propylenediamine have been made by a number of workers⁴²⁻⁵⁶. All the complexes have been found to be reversibly reducible at the DME. Miura and coworkers⁵⁷ investigated the Cu (II) complexes with aminoacids like histidine, glycine, alanine, aspartic acid and glutamic acid by polarographic method and arrived at the conclusion that in each case a 1 : 2 complex is formed. Li and Manning⁵⁸ have reported the formation constants of complexes of Pb (II) and Cd (II) with cysteine, glutamine, histidine and methionine. Similarly, Kostromin and Vekslina⁵⁹ have studied the complex of Cd (II) with glycine and α - alanine to detect the presence of $[Cd (gly)_2]$ and $[Cd (\alpha - ala)_2]$ species in solution even in presence of low

concentration of amino acid anion. The interaction of Cu (II) with asparagine has been studied polarographically by Malik et al⁶⁰ to determine the composition and stability constants of complexes so formed. In a similar vein, Bapna and Karmalkar⁶¹ and McKenzie and Mellor⁶² have studied the Pb (II) - glycine system at the DME to report the formation of multiple 1 : 1 and 1 : 2 and single 1 : 1 complex respectively.

The polarographic behaviour of Pb (II) - glutamate system has also been investigated by the polarographic method by Lai and Chang⁶³. They have reported the formation of a number of hydroxy complexes. Smith et al⁶⁴ having polarographically studied complexes of Cu (II) with glycine, α - alanine, β - alanine, phenylalanine, γ - aminobutyric acid, leucine and valine, and made an attempt to discuss the effect of chelating ring size and other steric factors on the stability of the corresponding complex species. A comprehensive account of polarography of complexes of Pb (II) and Cu (II) with glycine, DL - α - alanine, and DL - β - alanine, DL - valine, L - asparagine, DL - aspartic acid and L - glutamic acid has been provided by Rao and Subrahmanya⁶⁵⁻⁶⁸ after an extensive study.

The versatile method of polarography has once again been utilised by Radhakrishnan and co-workers⁶⁹ to find out and report the stability constants of Cd (II) complexes with alanine. On the same lines Shibata et al⁷⁰. Have polarographically determined the formation constants of Cd (II) - glutamate and Cd (II) - asparaginate complex species. Quintin and Foglizzo⁷¹ have investigated the chelate formation by L - tryptophan with Cu (II) and Pb (II). The polarographic behaviour of Cd (II) and Pb (II) with threonine in aqueous and aquo - non - aqueous media has been

studied by Rawat and Gupta⁷² while Kapoor and Kishan⁷³ have used polarography as well potentiometry to study the formation of complex species by N, N - dihydroxy ethylglycine with Pb (II) at different pH values. They came to the conclusion that 1 : 1 and 1 : 2 chelate are formed. The 1 - hydroxyproline complexes with Cu (II) have been investigated polarographically by Haq and Khan⁷⁴. They observed that the reduction at the DME was irreversible. The complexes of some divalent metal ions with propylenediamine have been studied at the DME by Maheswari and co - workers⁷⁵ to reveal that Cd (II) and Cu (II) form 1 : 1, 1 : 2 and 1 : 3 stepwise complexes while Pb (II) forms only 1 : 1 and 1 : 2 complexes. Rangarajan et al⁷⁶ have polarographically studied the methionine complexes of Cd (II) in aquo - non - aqueous solution of ethanol, methanol and dioxan. Prabhu and co - workers⁷⁷ have undertaken the polarographic study of proline complexes of Cu (II) to observe that 1 : 1 and 1 : 2 complexes that are formed undergo quasi - reversible reduction. Patil and Nemade⁷⁸ have also used polarography to study Cu (II) complexes with arginine in aquo-methanol and - ethanol media. They found that the 1 : 1 and 1 : 2 complexes formed in solution are reversibly reduced at the DME. Khuspe and Nemade⁷⁹ have investigated the complexes of Cd (II) with glutamic acid, norvaline, and isoleucine by their reduction at the DME and found out the formation constants of the complexes so formed. The polarographic study of Pb (II) complexes with asparagine, phenylalanine and tryptophan by Patil et al⁸⁰ has revealed that while asparagine forms 1 : 1, 1 : 2 and 1 : 3 complex species, phenylalanine and tryptophan can form only 1 : 1 and 1 : 2 complexes.

The polarographic study of complexes of Pb (II) with glycine, L - glutamine and L - asparagine with a view to determine the formation constants has been carried out by Khan and Nema⁸¹. Similarly, Nair et al⁸² have studied the amino acid complexes of Cu (II) and reported the stability constants of complexes formed in solution.

1.02.02 STUDIES ON MIXED LIGAND COMPLEXES

During the past three decades there has been a spurt in the studies on phenomenon of mixed ligand complex formation in which more than one type of ligand, other than the solvent molecules is linked directly to the central metal ion to yield a species with the general formula $[MX_i Y_j Z_k \dots\dots\dots]$. Earlier studies⁸³⁻⁹³ made use of spectrophotometry to investigate such complexes. A number of researchers have also used potentiometric measurements^{83,84,94,95}, and pHmetric titration data^{84,96-99} to study this unique phenomenon, specially the ternary complex formation. It has been concluded from the aforementioned studies and on the basis of statistical considerations that mixed ligand complex formation usually takes place when two or more different kind of ligands are present in a solution of a metal ion. It may be noted here that it is worthwhile to study mixed complexes whenever the concentrations of ligands involved are such that the products of the stability constant for simple complexes and concentration of the ligands, raised to the appropriate power are comparable, Thus,

$$\beta_{MX_i} [x]^i \approx \beta_{MY_j} [y]^j \approx \beta_{MZ_k} [z]^k \approx \dots\dots\dots$$

Schaap and McMasters¹⁰⁰ (1961) were the first to apply the method of polarography to the study of mixed ligand complexes by devising a logical extension of the method of Deford and Hume¹⁰ for the study of

simple complexes which reduce reversibly at the DME. Consequently, a number of investigators have applied the method to determine the formation constants of mixed ligand complexes in solution.

In most cases, the metal ions taken were Cd (II), Cu (II) and Pb (II) because generally, their reduction is reversible and diffusion controlled. Thus Sunderesan and Sundaram¹⁰¹ have studied the mixed ligand complex formation of Cu (II) with glycine and α - alanine. Kidani et al¹⁰² have carried out the study of Cu (II) complexes with histidine and δ - hydroxyquinoline - 5 - sulphonic acid at varying pH. The mixed complexes of Pb (II), Cu (II) and Cd (II) with histidine and hydroxide ions in the pH range 9-13 have been studied by Kim et al¹⁰³, Jain, Kishan and Kapoor¹⁰⁴ have investigated the Cd (II) - bionate-glycinate system polarographically. A number of other researchers¹⁰⁵⁻¹¹⁰ have taken amino acids as the primary ligands and 2, 2' - bipyridyl as the secondary ligand to study the ternary complexes of Cd (II).

The study of mixed ligand complexes of Cu (II) with heterodonor of the type [AB] with A is hydroxy carboxylic acids like lactic acid and B is an α or β - amino acid has been undertaken by Ramanujam and Krishnan¹¹¹. Again Sundaresan et al¹¹² have carried out polarographic studies to determine the composition and stability constants of Cd (II) with glycine and methionine. A series of studies¹¹³⁻¹¹⁵ were undertaken by Garg et al¹¹³⁻¹¹⁸ to study the mixed complexes of Cd (II) and Pb (II) with some carboxylic acids and ethylenediamine and propylenediamine. The ligand being bidentate, a maximum of three link themselves to the metal ion in differing proportions at different concentrations. Garg et al¹¹⁹ have also

studied the mixed complexes of these metal ions with phthalic acid and propylenediamine. They came to the conclusion that Cu (II) can attain of maximum coordination number of 4 while Cd (II) and Pb (II) can have 6 as their maximum co-ordination number.

Gupta and Co workers¹²⁰⁻¹²² have used amino acids as the primary ligands and pyridoxine and ascorbic acids as secondary ligands to carry out the polarography of Cd (II) complexes. Saxena et al¹²³⁻¹²⁴ have carried out polarography of Cu (II) and Pb (II) with similar ligands. They have observed that a 1 : 1 : 1 complex is formed in each case. The study of mixed ligand complexes of Cd (II) with amino acids as primary ligands and carboxylic acids as secondary ligands have been undertaken by Khan and Nema¹²⁵⁻¹²⁷. There is also a report¹²⁸ on the polarographic study of mixed ligand complexes of Pb (II) with pyridoxine and amino acids. On the same lines, mixed complexes of Cu (II) with carboxylic acids as primary ligands and amino acids as the secondary ligands have been studied polarographically by Bhattacharya et al¹²⁹. Similarly, Manjula and co-workers¹³⁰ have investigated the complexes of Cu (II) with histidine as the primary ligand and other amino acids as the secondary ligands. Neema and Khan¹³¹ have reported their study on Cd (II) mixed complex with amino acids as primary ligands and propionic acid as the secondary ligand. Alarjos and coworkers¹³² have studied the reduction of mixed complex formation by glycine and isoleucine with Cu (II) at the DME and found that only one 1 : 1 : 1 complex is formed. Some other studies¹³³⁻¹⁶³ are also reported in literature of mixed ligand complex formation by Cu (II), Cd (II) and Pb (II) ions with an amino acid as one of the ligands.

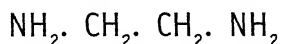
The foregoing survey of literature reveals that there are still gaps left in the knowledge of mixed ligand complexes of Cd (II), Cu (II) and Pb (II). One such gap comprises in the field of complexes of diamines and amino acids with these metal ions.

1.03 PLAN OF WORK

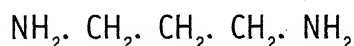
It was therefore deemed worthwhile and gainful to carry out a comprehensive polarographic investigation of the phenomenon of mixed ligand complex formation by Cd (II), Cu (II), and Pb (II) with diamines and aminoacids listed below :-

Diamines -

Ethylenediamine (en)



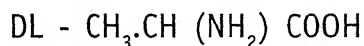
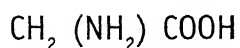
Propylenediamine (pn)



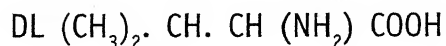
Amino acids -

Glycine (gly)

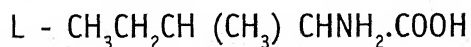
DL - Alanine (ala)



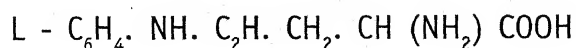
DL - Valine (val)



L - Isoleucine (isolc)



L - Tryptophan (try)



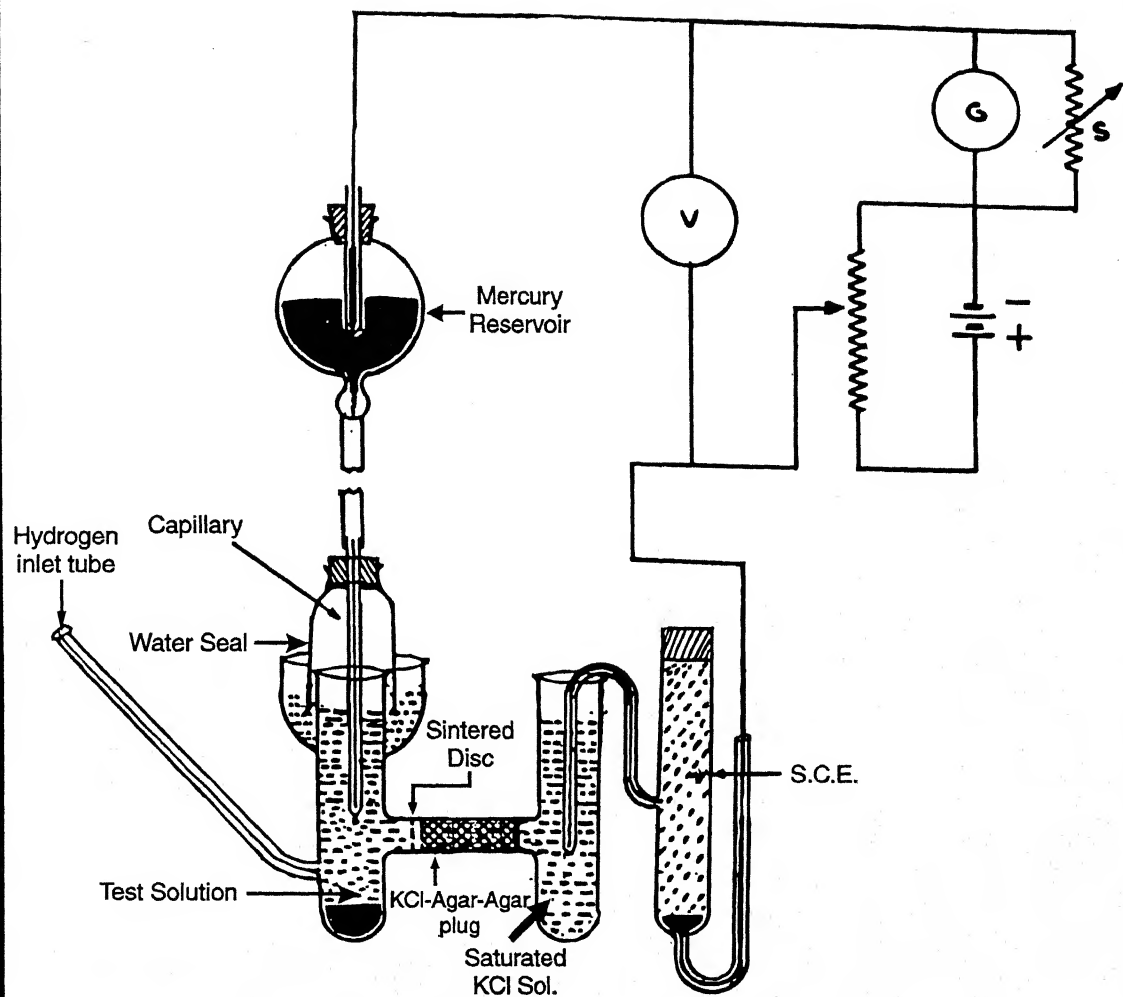


Fig. 1.01

POLAROGRAPHIC CIRCUIT WITH H - CELL

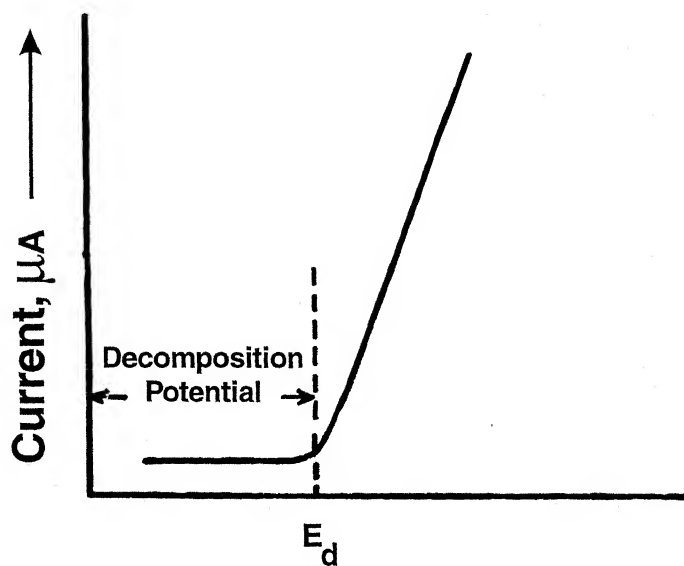


FIG. 1.02

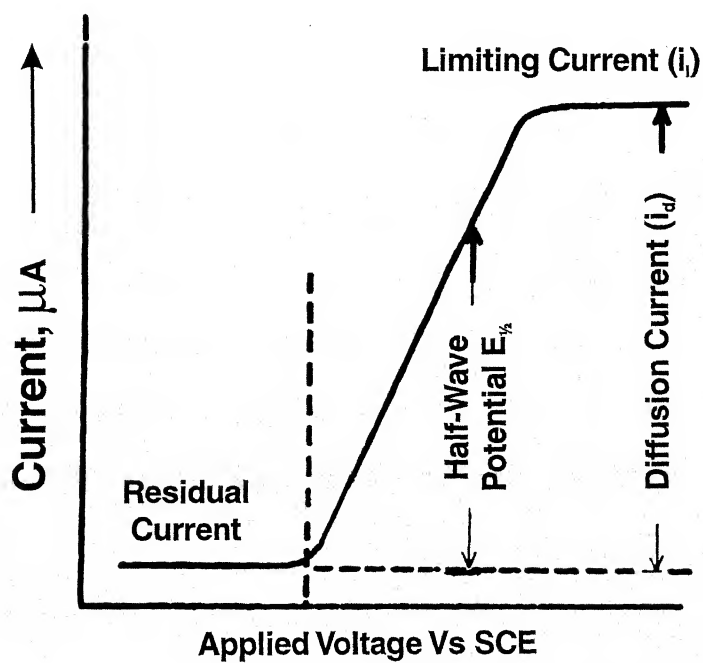


FIG. 1.03

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CHAPTER - II

EXPERIMENTAL AND

THEORETICAL ASPECTS

2.01 INTRODUCTION :

When a metal ion forms a complex in solution, its half wave potential ($E_{1/2}$) is usually shifted to the more negative side and diffusion current (i_d) decreases. The measure of this shift in $E_{1/2}$ as a function of free ligand concentration has been gainfully employed by Lingane¹, Kolthoff² and Crow³ to formulate methods to evaluate the stability constants of complexes formed in solution. But all these methods are derived from Nernst equation which is applicable for reversible systems alone. Hence, it must be emphasised here that these methods are employed only if the reduction of the complex species is reversible at the DME.

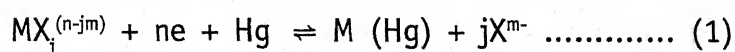
It is, therefore, essential to establish reversibility of the process occurring at the DME. Secondly, the formulation of equation for determination of stability constants assumes that the rate controlling step of the electrode process is diffusion controlled. Thus, it must also be ensured that the reducible species reaching the electrode do so by diffusion alone.

2.02 FORMULATION OF EQUATIONS FOR DETERMINATION OF STABILITY CONSTANSTS :

2.02.01 Lingane's method

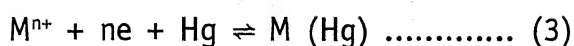
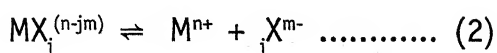
Lingane¹ has derived a method for the determination of stability constants of a complex which reduces reversibly at the DME.

The reduction of complexed metal ion to metallic state at the DME is represented by the following equilibrium.



Where MX_j is the complex ion of the metal ion M with ligand. X carrying a charge of - m. M (Hg) represents the amalgam formed at the

surface of the DME. The electrode reaction may be conveniently broken up into two partial reactions.



At 25°C, Lingane derived the following expression for the determination of the composition and formation constant β of the complex.

$$(E_{1/2})_s - (E_{1/2})_c = \Delta E_{1/2} = \frac{0.05915}{n} \log \beta + j \frac{0.05915}{n} \log C_x \dots\dots (4)$$

where $(E_{1/2})_s$ and $(E_{1/2})_c$ are the half wave potentials of the simple and the complexed ion respectively and C_x represents the ligand concentration. The plot of the left hand side of equation (4) against C_x yields a straight line, the intercept of which on the ordinate axis corresponding to $C_x = 1$ M or $\log C_x = 0$ yields the value of β .

The rate of change of $E_{1/2}$ with ligand concentration C_x may be expressed as

$$\frac{d(E_{1/2})_c}{d \log C_x} = -j \frac{0.05915}{n} \dots\dots\dots (5)$$

The plot of $(E_{1/2})_c$ vs $\log C_x$ is found to be linear in case of single complex formation with a slope of $j \frac{0.05915}{n}$. Thus value of j , the number of ligands molecules attached to the metal ion, is easily calculated and so is the stability constant.

2.02.02 DeFORD AND HUME METHOD :

The Lingane method suffers from the shortcoming that it is applicable when only one complex is formed in solution. If, however, the solution contains complexes with varying co-ordination numbers, the plot of $E_{1/2}$ vs $\log C_x$ is not linear. One gets a smooth curve. The Lingane's

equation fails.

For such successive complex formation, DeFord and Hume⁴ have formulated a method to determine their successive formation constants by the polarographic method. According to his method, an experimentally determinable function $F_0(X)$ is expressed as

$$F_0(X) = \text{antilog.} \left[\frac{0.4343nF}{RT} \Delta E_{1/2} + \log \frac{I_s}{I_c} \right] \dots (6)$$

Where,

I_s = Diffusion current constant of simple metal ion.

I_c = Diffusion current constant of the complexed ion at a free ligand concentration of $[X]$

$\Delta E_{1/2}$ = Cathodic shift in half wave potential of simple metal ion when $[X]$ mole of free ligand is present, and n , F , R , and T have their usual significance.

When an excess of ligand is present $C_x = [X]$ and at constant ionic strength, it has been shown that

$$F_0[X] = \beta_0 + \beta_1[X] + \beta_2[X]^2 + \dots \beta_n[X]^n \dots (7)$$

where β_0 is the stability of the zero complex and is taken as unity and $\beta_1, \beta_2, \dots, \beta_n$ are stability constants of 1 : 1, 1 : 2, ..., 1 : n metal to ligand ratio complexes respectively.

A graphical representation method due to Leden⁵ is applied to determine the numerical value of $\beta_1, \beta_2, \dots, \beta_n$ when $F_0[X]$ is plotted against $[X]$, a steeply rising curve in which near $[X] = 0$, the limiting slope has a value of β_1 , and the intercept on $F_0[X]$ axis has a value of $\beta_0 = 1$, one gets a preliminary value of β_1 . A new function $F_1(X)$ has been defined as

$$F_1(X) = \frac{F_0(X) - 1}{(X)} = \beta_1 + \beta_2 [X] + \dots \beta_n (X)^{n-1} \dots (8)$$

Again a plot of $F_1(X)$ vs $[X]$ has a limiting slope of β_2 as $[X]$ approaches zero and β_1 as the intercept on the $F_0(X)$ axis. This is confirmative value of β_1 while that of β_2 is only tentative. A new function $F_2[X]$ is similarly defined by the expression

$$F_2(X) = \frac{F_1(X) - \beta_1}{[X]} = \beta_2 + \beta_3 [X] + \dots \beta_n [X]^{n-2} \dots (9)$$

The computation of the successive formation constants is continued till all the β values are obtained. Thus for the penultimate complex MX_{n-1} , the $F_{n-1}(X)$ function is given by the relation.

$$F_{n-1}(X) = \frac{F_{n-1}(X) - \beta_{n-2}}{[X]} = \beta_{n-1} + \beta_n [X] \dots (10)$$

For obvious reasons, the plot of $F_{n-1}(X)$ vs $[X]$ is linear indicating that the penultimate function has been reached. The intercept on the $F_{n-1}(X)$ equals β_{n-1} while the slope of the linear curve yields the tentative β_n value.

The final $F_n(X)$ function becomes independent of the ligand concentration as represented by the following equation

$$F_n(X) = \frac{F_{n-1}(X) - \beta_{n-1}}{[X]} = \beta_n \dots (11)$$

A straight line parallel to the $[X]$ axis is obtained for the $F_n(X)$ vs $[X]$ plot, The intercept on $F_n(X)$ axis yields the value of β_n . Improvements as suggested by Irving⁶ are taken into consideration & for all such computations.

2.02.03 SCHAAP AND McMASTERS METHOD

In order to determine the formation constant of mixed ligand complex species which reduce reversibly at the DME, Schaap and Mc Masters⁷ have devised a logical extension of the DeFord and Hume method described in the previous subsection.

A complex species may be formed in solution as per the equilibria



Where i and j are stoichiometry numbers of two different ligands X and Y respectively linked simultaneously to the metal M.

Schaap and McMasters extended the $F_0(X)$ of DeFord and Hume to define a new function $F_{00}(X,Y)$ as

$$F_{00}(X,Y) = \sum \beta_{ix_j} [X]^i [Y]^j \dots\dots\dots (13)$$

In terms of experimentally measurable data, the $F_{00}(X,Y)$ function can be written as

$$F_{00}(X,Y) = \text{antilog.} \left[\frac{0.4343nF}{RT} \Delta E_{1/2} + \log \frac{I_m}{I_c} \right] \dots (14)$$

The $F_{00}(X,Y)$ function may be factorised as follows

$$\begin{aligned} F_0(X,Y) = & \{ \beta_{00} + \beta_{01} [Y] + \beta_{02} [Y]^2 + \beta_{03} [Y]^3 \} [X]^0 \\ & + \{ \beta_{10} + \beta_{11} [Y] + \beta_{12} [Y]^2 \} [X]^1 \\ & + \{ \beta_{20} + \beta_{21} [Y] \} [X]^2 \\ & + \{ \beta_{30} \} [X]^3 \dots\dots\dots (15) \end{aligned}$$

Of the two ligands, the concentration of Y is kept constant while that of X is varied.

The situation could be reversed if the concentration X is kept constant and that of Y is varied to yield on alternative function $F_{00}(X,Y)$ as follows.

$$\begin{aligned}
F_{00} [X,Y] &= \{\beta_{00} + \beta_{10} [X] + \beta_{20} [X]^2 + \beta_{30} [X]^3\} [Y]^0 \\
&+ \{\beta_{01} + \beta_{11} [X] + \beta_{21} [X]^2\} [Y]^1 \\
&+ \{\beta_{02} + \beta_{12} [X]\} [Y]^2 \\
&+ \{\beta_{03}\} [Y]^3 \dots\dots\dots (16)
\end{aligned}$$

where the β values stand for the stability constant of corresponding simple and complex species. Equation (15) and (16) may also written as

$$F_0 [X,Y] = A + B [X] + C [X]^2 + D [X]^3 \dots\dots\dots (17)$$

and

$$F_{00} [X,Y] = A' + B' [X] + C' [Y]^2 + D' [Y]^3 \dots\dots\dots (18)$$

Where for a given value of $[Y]$, A, B, C and D are constant values and for a given value of $[X]$, A', B', C' and D' are constant.

The magnitude of A can be calculated at a given $[Y]$ value if the successive stability constants of simple complexes of metal ion with Y alone are known under identical conditions. A comparison of this value of A with value obtained by a plot of F_{00} vs $[X]$ at some value of $[Y]$ where the intercept on F_{00} axis equals A corresponding to $[X] = 0$

A new function F_{10} may then be defined as follows

$$F_{10} = \frac{F_{00} - A}{[X]} = B + C [X] + D [X]^2 \dots\dots\dots (19)$$

Again the intercept on the F_{10} axis yields the value B in a plot of F_{10} vs $[X]$

When the procedure is continued further, F_{20} function is defined as

$$F_{20} = \frac{F_{10} - \beta}{(X)} = C + D [X] \dots\dots\dots (20)$$

The plot of F_{20} vs $[X]$ is found to be linear with the intercept on the F_{20} axis equalling C and its slope being the value of D .

The value of C so obtained is gainfully employed to determine the mixed stability constant β_{21} as per equation (15) since β_{20} is known for the simple system. In order to evaluate the mixed formation constants β_{11} and β_{12} , one needs determination of B at two different $[Y]$ values to obtain two simultaneous equations.

2.03 EXPERIMENTAL

A manual Toshniwal Cl-49 potentiometer in combination with a DME was used throughout the investigations.

2.03.01 POLARISED MICROELECTRODE

The dropping mercury electrode (DME) was a fine glass capillary with a uniform internal diameter of 0.05 mm. The capillary was linked to the mercury reservoir through a polythene tubing. It was possible to adjust the height of the mercury column to any desired level by lowering or raising the reservoir. A platinum electrode was dipped in mercury reservoir for electrical contact.

Mercury of very high purity was used to serve as DME. Distilled mercury was washed with 10% HNO_3 a number of times before being thoroughly washed with water to remove nitric acid and other impurities. It was dried, filtered and distilled under reduced pressure.

2.03.02 REFERENCE ELECTRODE

A Saturated Calomel Electrode (SCE) was used as the reference electrode. All potentials reported in this dissertation have been measured taking SCE as the standard electrode.

2.03.03 SALT BRIDGE

A potassium chloride - Agar - Agar bridge was used to link the SCE to the reaction half cell.

2.03.04 POLAROGRAPHIC CELL

An H type cell (Fig. 2.01) was used. The half reaction cell part consisted of a flat bottomed pyrex tube. DME could be inserted into the cell through a clean rubber cork with a hole at the centre.

2.03.05 HYDROGEN ASSEMBLY

The dissolved oxygen in test solution was removed by passage of hydrogen gas for 15 minutes prior to recording of a polarogram. Otherwise, reduction waves for oxygen are also obtained¹⁹. The hydrogen gas required for the purpose was generated in a Kipp's apparatus charged with Analar Zinc metal and dil. HCl. The evolved gas was purified²⁰ by passing it through four bottles in succession. The bottles contained alkaline KMnO_4 solution, Lead acetate solution, dilute silver nitrate solution and distilled water in the order stated.

2.03.06 THERMOSTAT

The polarographic cell and the SCE were thermostated at the desired temperature by placing them in trough containing water fitted with a low speed stirrer and a heating element, relay and a toluene regulator. Temperature could be measured with an accuracy of $\pm 0.1^\circ\text{C}$.

2.04 METHODS, MATERIALS AND PROCEDURES

2.04.01 DETERMINATION OF CAPILLARY CHARACTERISTICS

In order to determine the rate of flow of mercury 'm', the mercury of DME was allowed to flowout for a given period of time in presence of

the electrolyte used in an open circuit²¹. The amount of mercury so obtained was dried and weighed.

Similarly the drop time 't' was calculated by noting the time for a definite number of drops of fall off the DME at the given height of the mercury column.

2.04.02 MATERIALS

For all experimental work, freshly prepared conductivity water was used. The purity of the conductivity water was ensured by determination of its conductivity and pH. All chemicals of analytical grade purity were used.

2.04.03 RECORDING OF A POLAROGRAM

The requisite amounts of the depolarizer ions, ligand, supporting electrolyte and the maxima suppressor were added to a 25 ml measuring flask from the stock solution. The solution was made up to the mark with conductivity water. It was transferred to the polarographic H - cell and was deaerated for about 15 minutes by bubbling purified hydrogen gas through the solution. The DME was inserted into the test solution, circuit completed by connecting the SCE through the salt bridge. The voltage was increased by 0.1 V in each step and current was noted at each stage. The polarogram was obtained by plotting values of observed current against the applied potential.

2.05 THEORETICAL ASPECTS

2.05.01 DIFFUSION CONTROLLED REDUCTION AT THE DME

Ilcovic equation can be written in the following form if one consider the instantaneous current at any time during the life of the

mercury drop.

$$i_d = 706 n C D^{1/2} m^{2/3} t^{1/6} \dots\dots\dots (33)$$

where n C and D concern the solution factors while m and t characterise the electrode (DME) factors.

On keeping the solution factors constant, Ilcovic equation becomes

$$i_d = \text{constant } m^{2/3} t^{1/6} \dots\dots\dots (34)$$

Poiseuille's theorem states that the rate of flow of a liquid through a capillary is directly proportional to the corrected height (h_{corr}) of the liquid column. One can say that the rate of flow (v) of mercury through DME is proportional to 'm' which is proportional to h_{corr} . In addition, v is proportional to $1/t$. Therefore, $i_d = \text{constant } h_{\text{corr}}^{2/3} t^{1/6} = \text{constant } h_{\text{corr}}^{1/2} \dots\dots\dots$. This relationship forms the basis of finding out the diffusion controlled nature of the polarographic reduction. The h_{corr} is the height of the mercury column corrected for back pressure due to interfacial tension at the surface of the drop. Thus.

$$h_{\text{corr}} = h_{\text{Hg}} - (3.1/m^{1/3} t^{1/3}) \dots\dots\dots (35)$$

If one can keep the electrode characteristics and also the nature of the solution constant, then $i_d \propto C$. This forms basis for determining the diffusion controlled nature of the reduction at the DME.

2.05.02 REVERSIBILITY OF THE REDUCTION AT THE DME

The 'log plots' are the most widely used tool for establishing the reversible character of a reduction at the DME. At 25°C, for a reversible electrode reaction the following equation holds good.

$$E_{\text{de}} = E_{1/2} - \frac{0.05915}{n} \log \frac{i}{i_d - i} \dots\dots\dots (36)$$

It is obvious that the plot of E_{de} vs $\log i/i_d - i$ should be linear

(34)

with a shape of $\frac{59.15}{n}$ mV. The potential at which the linear plot intersects the E_{de} axis corresponds to the $E_{1/2}$ of the reversible reduction process.

In an alternative scheme, the $E_{1/2}$ and $E_{3/4}$ values are measured from the recorded polarogram. These two potentials correspond respectively to the E_{de} at which the current is equal to one fourth and three fourth of the diffusion current. Thus

$$\begin{aligned} E_{1/4} &= E_{1/2} - \frac{0.05915}{n} \log \frac{i_d/4}{i_d - i_d/4} \\ &= E_{1/2} - \frac{0.05915}{n} \log 1/3 \dots\dots\dots (37) \end{aligned}$$

Similarly

$$E_{3/4} = E_{1/2} - \frac{0.05915}{n} \log 3 \dots\dots\dots (38)$$

So that

$$\begin{aligned} E_{3/4} - E_{1/4} &= - \frac{0.05915}{n} \log 9 = - \frac{0.0564}{n} \dots\dots (39) \\ &\text{at } 25^\circ\text{C} \end{aligned}$$

It becomes evident from equation (39) that ' $E_{3/4} - E_{1/4}$ ' for a reversible cathodic wave is of the order of $- 56.4/n$ mV and for a reversible anodic wave it approximates $+ 56.4/n$ mV.

It must be noted here that the slopes of the log plots and ' $E_{3/4} - E_{1/4}$ ' values can be used to conclude with certainty that an electrode process is irreversible if there is considerable deviation from the expected values. Even if the slope of log plots tally with $59.2/n$ mV and the numerical value of ' $E_{3/4} - E_{1/4}$ ' is near $56.4/n$ mV, the process could still be irreversible²².

The irreversibility of an electrode process is, however, better

ascertained²³ by using the height of the mercury column (h_{corr}) as discussed in the following lines.

As for the irreversible²⁴ waves, there is progressive transition in dependence of the current on the effective height of the mercury column. The initial current at the foot of the wave is independent of h_{corr} i.e. the current is kinetically controlled. The final current at the top of the wave is proportional to the square root of the effective height $h_{\text{corr}}^{1/2}$. On the other hand the current is proportional to $h_{\text{corr}}^{1/2}$ at any point of reversible polarographic wave.

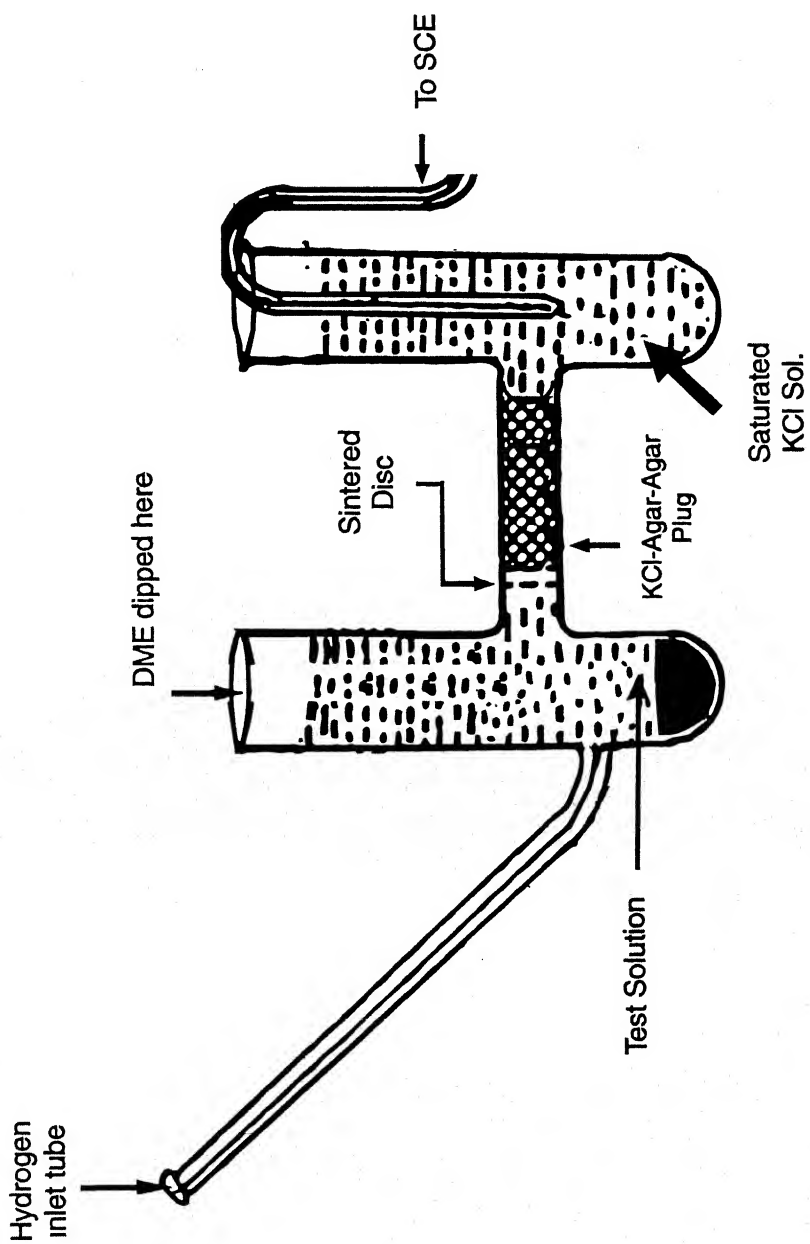


Fig. 2.01

POLAROGRAPHIC H - CELL

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CHAPTER - III

CADMIUM

COMPLEXES

3.01 INTRODUCTION :

A number of our investigators¹⁻⁶ have carried out of the polarographic studies on ternary complex formation by Cd (II) with amino acids and nitrogen bases. They have normally taken amino acids as the primary ligands and 2, 2' bipyridyl as the secondary ligand. Many researchers⁷⁻¹⁹ have also reported the formation of various other mixed ligands of Cd (II) taking amino acids as one the ligands. As far as the use of diamines as the primary ligands is concerned, only Ramaiah, Bhat and Sudaresan²⁰ have made a worthwhile contribution by investigating the Cd (II) - ethylenediamine - glycine system by the reduction at the dropping mercury electrode. Under the circumstances, it was thought necessary to undertake intensive and extensive studies on the following systems with Cd (II) and diamines along with amino acids as ligands.

- (a) Cd (II) - ethylenediamine - glycine
- (b) Cd (II) - ethylenediamine - DL - alanine
- (c) Cd (II) - ethylenediamine - DL - valine
- (d) Cd (II) - ethylenediamine - L - isoleucine
- (e) Cd (II) - ethylenediamine - L - tryptophan
- (f) Cd (II) - propylenediamine - glycine
- (g) Cd (II) - propylenediamine - DL - alanine
- (h) Cd (II) - propylenediamine - DL - valine
- (i) Cd (II) - propylenediamine - L - isoleucine
- (j) Cd (II) - propylenediamine - L - tryptophan

3.02. EXPERIMENTAL

Only the analytical reagent grade chemicals were used and only

doubled distilled water was used to prepare and dilute solutions. Sodium nitrate was used to maintain ionic strength constant at 1.0 M. Maxima suppresser was not added to any test solution as no maxima was observed for the systems under investigation. As described in chapter II, the concentration of the ligand was increased while keeping the ionic strength and pH constant, the polarograms of the test solutions recorded. All measurements were made at $25 \pm 0.1^\circ\text{C}$. All recorded current and potential values were corrected for residual current and iR drop of the cell respectively.

Capillary characteristics of the DME were as follows :

$$m = 2.40 \text{ mg/sec, } t = 3.10 \text{ sec.}$$

The pH of test solutions was adjusted by adding requisite amount of dilute NaOH or HCl using a Toshniwal Cl - 49 pH meter.

n, the number of electrons involved in the reduction at DME of Cd (II) in presence of different ligands was determined as already described²¹ in Chapter II. In each and every case, the value of n was found to be 2.

3.03 RESULTS AND DISCUSSION

3.03.01 DETERMINATION OF pKa VALUES

Titration method due to Chaberek and Martell²² which utilises a glass electrode, was used to determine the pKa values of the ligands under study. The following values were obtained at $\mu = 1.0\text{m}$ and 25°C .

Ligand	abbreviation		pKa
ethylenediamine	en	pK ₁	7.05
		pK ₂	10.10
propylenediamine	pn	pK ₁	7.00
		pK ₂	9.50

glycine	gly	pK ₁	2.36
		pK ₂	9.78
DL - alanine	ala	pK ₁	2.10
		pK ₂	9.87
DL - valine	val	pK ₁	2.32
		pK ₂	9.72
L - isoleucine	isole	pK ₁	2.50
		pK ₂	9.75
L - tryptophan	try	pK ₁	2.83
		pK ₂	9.39

The pK_a values, as obtained above are in good agreement with literature values²³⁻²⁴.

These pK_a values in conjunction with pH values were used to determine the free ligand concentration of the test solution.

Table 3.01 to 3.17 contain the experimental data for the simple and ternary complex systems of Cd (II).

3.03.02 NATURE OF POLAROGRAPHIC WAVES

In each and every case Cd (II) gave a well defined polarographic waves in varying concentrations of ethylenediamine (en), propylene diamine (pn), glycine (gly), DL - alanine (ala), DL - valine (val), L - isoleucine (isole) and L - tryptophan (try) present singly or in combination. In each case the reduction was found to be entirely diffusion controlled as borne out by the linear nature of i_d vs $h_{corr}^{1/2}$ plots and their passing through the origin.

The reduction in each case was also found to be reversible - an

inference²⁵ drawn from the linearity of plots of $\log i/i_d - i$ vs E_{de} with slopes of the order of 31 ± 2 mV.

3.03.03 COMPOSITION AND STABILITY OF SIMPLE COMPLEXES

It was deemed essential to determine the composition and stability constants of simple complexes of cadmium (II) with ethylene diamine (en), propylenediamine (pn) glycine (gly), DL - alanine (ala), DL - valine (val), L - isoleucine (isoc) and L - tryptophan (try) separately before their mixed ligand complexes were investigated. However, identical conditions were maintained for both simple and mixed complex systems.

Solutions containing 10×10^{-3} M Cd (II), 0.1 M en and also 1.0×10^{-3} M Cd (II) with 0.1 M pn and ionic strength of 1.0 (NaNO_3) were polarographically examined at varying pH. There was a perceptible change in $-E_{1/2}$ with change in pH. It was observed that $-E_{1/2}$ was maximum at pH 8.2 for both the ligands. It was for this reason that this pH was selected to study the simple as well as mixed complexes. Obviously OH^- ions are unable to compete with en and pn to enter the coordination sphere.

Tables 3.01 to 3.07 contain the polarographic data of simple Cd(II) - en, Cd(II) - pn, Cd(II) - gly, Cd(II)- ala, Cd(II) - val, Cd(II)- isoc and Cd(II) - try . Fig. 3.01 to 3.07 depict the polarographic waves of the corresponding simple systems. In each case, there is a cathodic shift as well as decrease in diffusion current with increase in ligand concentration. It indicates complex formation. Except in the case of Cd (II) - try system, the plots of $\log [\text{ligand}]$ vs. $E_{1/2}$ are smooth curves indicating successive complex formation. Hence the method of DeFord and Hume²⁶ was applied to determine the stability of three successive complexes in each case as

depicted in figure 3.08 to 3.19.

In the case of Cd (II) - try however, the log (try) vs $E_{1/2}$ plot yields a strength line (Fig. 3.20). Hence formation of only complex was concluded. Its composition and stability was determined by Lingane's method²⁷.

The composition and stability constants of complexes so obtained are summarised below

System	composition	Stability	Constant	
		$\log\beta_1$	$\log\beta_2$	$\log\beta_3$
Cd (II) - en	1:1, 1:2, 1:3	6.14	9.91	12.35
Cd (II) - pn	1:1, 1:2, 1:3	6.44	9.81	12.27
Cd (II) - gly	1:1, 1:2, 1:3	4.34	7.47	10.50
Cd (II) - ala	1:1, 1:2, 1:3	4.30	7.38	9.47
Cd (II) - val	1:1, 1:2, 1:3	4.11	7.11	9.69
Cd (II) - isola	1:1, 1:2, 1:3	4.20	7.13	9.90
Cd (II) - try	— 1:2 —	—	8.85	—

3.03.04 COMPOSITION AND STABILITY OF MIXED COMPLEXES

In order to determine the composition and stability constants of mixed ligand complexes, a ligand displacement technique was used and the method of Schaap and McMasters²⁸ applied. In these mixed ligand systems too, the reduction was found to be reversible involving 2 electrons and entirely diffusion controlled (Fig. 3.21 to 3.30).

(A) Cd (II) - ETHYLENEDIAMINE - GLYCINE SYSTEM

In the system, [gly] was kept constant 0.01 M and the concentration of ethylenediamine varied from 0 to 12×10^{-3} M. Polarography

of such solutions revealed that $E_{1/2}$ exhibits greater cathodic shift²⁹ than that in absence of glycine as depicted in fig. 3.01 and 3.21. It indicated mixed ligand complex formation by glycinate ion and ethylenediamine with Cd (II) ion. The procedure was repeated at $[gly] = 0.02$ M. The polarographic data at the two fixed concentration of $[gly]$ is presented in table 3.08 and illustrated in figure 3.31. From the plots F_{ij} vs $[en]$, the values of the constants^{28,30} obtained as follows

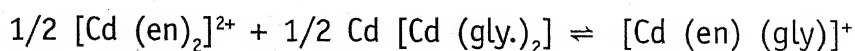
	log A	log B	log C	loc D
At $[gly] = 0.01$ M	3.84	7.07	12.23	14.40
At $[gly] = 0.02$ M	3.90	7.32	10.25	12.38

From the values of A, B, C and D the mixed complex stability constant values were calculated to be $\beta_{11} = \log 10.79$ for $[Cd(en)(gly)]^+$ and $\beta_{21} = \log 12.32$ for $[Cd(en)_2(gly)]^+$ complex.

However a negative value of β_{12} was obtained ruling out the possibility of formation of $[Cd(en)(gly)_2]$ mixed complex.

Flowsheet diagram 3.01 conveniently summarises the results values are logarithms of equilibrium constant of the reactions indicate by the arrow.

The mixing constant $K_M^{15,20,29,31,32}$ for the reaction

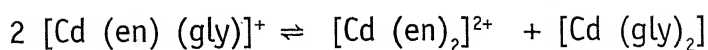


can be calculated from the following relation.

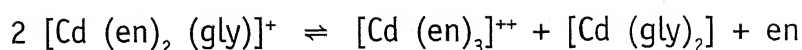
$$\log K_M = \log \beta_{11} - 1/2 \log (\log \beta_{20} + \log \beta_{02})$$

In the present system the $\log K_M$ value has been found to be + 2.1 indicating that the mixed 1 : 1 : 1 complex is more stable than the two binary 1 : 2 complexes.

In the following diproportionation reaction.



and



the equilibrium constants have been found to be - 4.20 and - 5.22 respectively. It once again shows that ternary complexes are much stronger than binary complexes for the metal ion and the ligands under investigation.

(B) Cd (II) - ETHYLENEDIAMINE - DL - ALANINE SYSTEM

Two sets of polarographic data were obtained by keeping [ala] constant at 0.02 and 0.04 M and varying the ethylenediamine concentrations. In both the sets, the cathodic shift in $E_{1/2}$ was more than that in simple complexes at the same ligand concentration [table 3.01 and 3.09] indicating that mixed ligand complex formation had taken place.

F_{ij} [X,Y] functions were computed for both the sets. The same are presented table 3.09 and fig. 3.32. The plots of F_{ij} [X,Y] vs [en] at the two concentrations yield the following values of A, B, C, and D.

[ala]	log A	log B	log C	log D
0.02 M	3.77	7.04	10.28	12.30
0.04 M	3.90	7.20	10.32	12.34

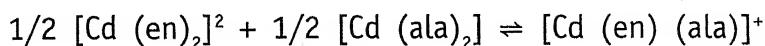
From these values of A, B, C and D, β_{12} corresponding to the $[\text{Cd}(\text{en})(\text{ala})_2]$ was found to have a negative value indicating that complex is so unstable that its existence can be ruled out.

The formation constants of other ternary complexes are listed below

$$[\text{Cd (en) (ala)}]^+ \quad \log \beta_{11} = 10.47$$

$$[\text{Cd (en)}_2 \text{ (ala)}]^+ \quad \log \beta_{21} = 12.62$$

The flowsheet diagram 3.02 gives a summary of simple and ternary stepwise complex formation process which took place during the experiments. The numerical values are the logarithm value of equilibrium constant of the reaction indicated by the arrow concerned. For the equilibrium

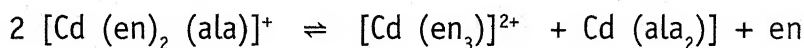
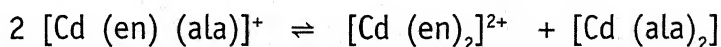


the mixing constant K_M can be computed from the reaction.

$$\log K_M = \log \beta_{11} - 1/2 [\log \beta_{20} + \log \beta_{02}]$$

Its value has been found to be + 1.82. It conclusively indicates that $[\text{Cd (en) (ala)}]^+$ is more stable than the two parent 1 : 2 binary complexes.

The equilibrium constants for the following disproportionation reactions were also determined.



There values were found to be - 3.65 and - 5.51 respectively. It again indicates that the formation of mixed complexes is more strongly favoured than that of simple complexes in the system under investigation.

(C) Cd (II) - ETHYLENEDIAMINE - DL - VALINE SYSTEM

The [val] was kept constant at 0.02 M and 0.02 M while concentration of ethylenediamine varied from 0.0 to 12×10^{-3} M in presence of Cd^{++} ions as stated earlier to obtain two sets of data for variation in $E_{1/2}$ with [en] It was noted that $E_{1/2}$ values were more negative in presence of DL - valine than in its absence (table 3.01 and 3.10). It indicated mixed

ligand complex formation by Cd (II) with valinate ion and ethylenediamine molecule. The polarographic functions $F_{ij} [X,Y]$ of the systems were used to evaluate A, B, C and D (Table 3.10 and fig. 3.33)

[val]	log A	log B	log C	log D
0.02 M	3.84	7.07	10.25	12.25
0.04 M	3.90	7.39	10.27	12.27

It was possible to determine the stability constants of the three ternary complexes formed

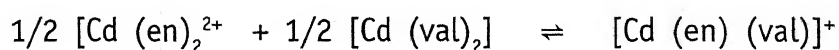
$$[\text{Cd (en) (val)}]^+ \quad \log \beta_{11} = 10.32$$

$$[\text{Cd (en) (val)}_2] \quad \log \beta_{12} = 11.62$$

$$[\text{Cd (en)}_2 \text{ (val)}]^+ \quad \log \beta_{21} = 12.22$$

It has been found convenient to summarise the results so obtained the flowsheet diagram 3.03 where numerical values indicate the logarithm of the equilibrium of the reaction.

As discussed in the previous system the mixing constant for the reaction

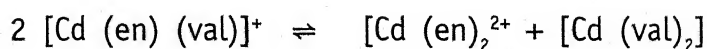


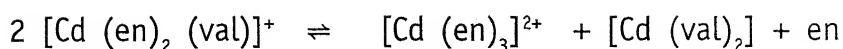
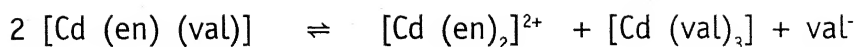
is computed from the equation

$$\log K_M = \log \beta_{11} - 1/2 (\log \beta_{20} + \log \beta_{02})$$

In this system it is + 1.81. The positive value makes it obvious that ternary 1 : 1 : 1 complex is more stable than the two binary parent 1 : 2 complex.

Further the values of disproportionation constants of the following reactions were computed.





Their values are - 3.62, - 3.64 and - 4.8 respectively. The large negative values further emphasise the point that ternary complexes are strongly favoured over binary complexes in this system.

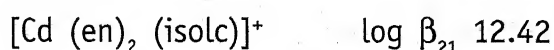
(D) Cd (II) - ETHYLENEDIAMINE - L - ISOLEUCINE SYSTEM

As in the previous system, the concentration of ethylenediamine was varied from 0.0 to 12×10^{-3} M keeping [isolc] constant at 0.01 M and 0.02 M for two series of test solutions. It was noticed that the cathodic shift in $E_{1/2}$ was more pronounced in presence of isoleucine than in its absence (Table 3.01 and 3.11). Mixed ligand complex formation was inferred by ethylenediamine and isoleucine with Cd (II).

The polarographic characteristics and F_{ij} [X,Y] functions (Table 3.11 and fig. 3.34) enabled the computation of A, B, C and D at the two isoleucine concentrations.

[isolc]	log A	log B	log C	log D
0.01 M	3.84	7.07	10.29	12.23
0.02 M	4.00	7.27	10.32	12.27

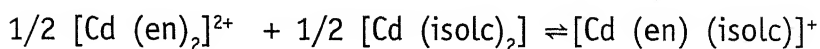
The values obtained as above facilitated the calculation of stability constants of mixed complexes.



β_{12} for $[\text{Cd} (\text{en}) (\text{isolc})_2]$ was found to have a negative value letting us infer that it is so unstable that it does not exist in solution under the experimental conditions.

Flowsheet diagram 3.04 summarises the possible equilibria with stability constants (logarithmic values) that occur in solution.

For the equilibrium.

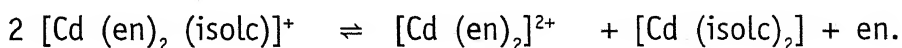
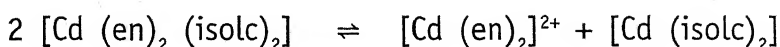


the K_M (mixing constant) can be evaluated from the relationship

$$\log K_M = \log \beta_{11} - 1/2 (\log \beta_{20} + \log \beta_{02})$$

Its value is found to be + 2.29. Obviously, therefore the mixed complex $[\text{Cd}(\text{en})(\text{isolc})]^+$ is more stable than the two parent binary 1 : 2 complexes.

For the disproportionation reactions



The equilibrium constants have been found to be - 4.58 and - 5.36 respectively. The large negative values indicate once again the formation of mixed complexes is favoured over simple ones in the system under investigation.

(E) Cd (II) - ETHYLENEDIAMINE - L - TRYPTOPHAN SYSTEM

The concentration of tryptophan was kept constant at 0.01 M and 0.02 M for the two series and that of ethylene diamine varied from 0.0 to 12×10^{-3} M.

The half wave potential values in the both series showed a more cathodic shift than that they showed in absence of tryptophan (Table 3.01 and 3.12). Mixed ligand complex formation was the conclusion. The plots of $\text{Fij. } [X,Y] \text{ vs } [\text{en}]$ (figure 3.35) at the two $[\text{try}]$ gave the following values of A, B, C and D.

[try]	log A	log B	log C	log D
0.01 M	3.84	7.09	10.21	12.23
0.02 M	3.95	7.30	10.26	12.32

From the above values of A, B, C and D, the mixed stability constants were computed. β_{12} corresponding to the complex Cd [(en)(try)₂] had a negative value. Hence its existence was ruled out. The other stability constant values are as follows :

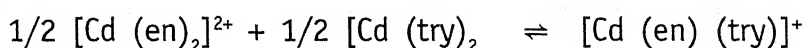
$$[\text{Cd (en) (try)}]^+ : \beta_{11} = 10.33$$

$$[\text{Cd (en)}_2 \text{ (try)}]^+ : \beta_{21} = 12.45$$

Flow sheet diagram 3.05 gives a graphic account of the relationship among the complexes formed in solution. The numerical values are indicative of logarithms of equilibrium constants for the reaction indicated by the concerned arrow.

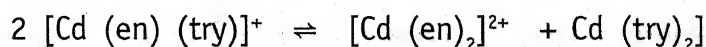
The equation

$\log K_M = \log \beta_{11} - 1/2 (\log \beta_{20} + \log \beta_{02})$ defined the mixing constant K_M for the reaction

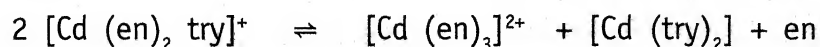


where in $K_M = + 0.95$ which indicates that the mixed complex form of 1 : 1 : 1 complex is strongly favoured over parent binary 1 : 2 complexes.

Similarly the disproportionation constants for the reactions



and



are evaluated as - 1.9 and - 3.7 respectively which also favour

formation of mixed complexes over simple complexes.

(F) Cd (II) - PROPYLENEDIAMINE - GLYCINE SYSTEM

Keeping the concentration of glycine constant at 0.01 M and 0.02 M respectively and varying the concentration of propylenediamine from 0.0 to 12×10^{-3} M, two series of polarographic data were obtained. It was noted that the cathodic shift in $E_{1/2}$ of Cd^{++} in presence of glycine was greater than that in its absence at each concentrations of propylenediamine (Table 3.02 and 3.13). Inferring complex formation, the F_{ij} [X,Y] functions were determined and values of constant A, B, C and D obtained for both series from Fig. 3.36.

[gly]	log A	log B	log C	log D
0.01 M	3.90	7.38	10.27	12.34
0.02 M	4.00	7.47	10.51	12.39

Consequently the stability constants of mixed complexes were evaluated.

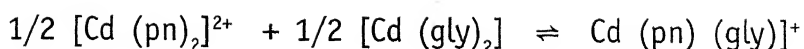
$$[\text{Cd (pn) (gly)}]^+ : \beta_{11} = 11.14$$

$$[\text{Cd (pn)}_2 \text{ (gly)}]^+ : \beta_{21} = 13.66$$

The value of corresponding to the complex $[\text{Cd (pn) (gly)}_2]$ was negative. It indicated that the complex does not exist in solution under the experimental conditions.

The flow sheet diagram 3.06 gives a graphic account of various complex species existing in solution and their relative stabilities. The numerical figures represent the logarithm of equilibrium constants of the reactions indicated by the concerned arrow mark.

The mixing constant K_M for the reaction

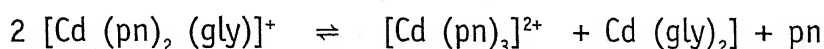


can be computed from the equation

$$\log K_M = \log \beta_{11} - 1/2 (\log \beta_{20} + \log \beta_{02})$$

The numerical value of K_M for the system has been found to be + 2.50. Decisively, therefore the ternary 1 : 1 : 1 complex is more stable than the parent 1 : 2 binary complexes.

Similar results are obtained from the disproportionation constant of the following reactions.



The constants are - 5.0 and - 7.58. The negative values once again suggested that formation of ternary complexes is strongly favoured over binary simple complexes.

(G) Cd (II) - PROPYLENEDIAMINE - DL - ALANINE SYSTEM

In this system, the concentration of propylenediamine was varied from 0.0 to 12×10^{-2} M keeping [ala] constant at 0.02 M and 0.04 M respectively for obtaining two sets of $E_{1/2}$ and i_d data. A greater cathodic shift in $E_{1/2}$ in presence of alanine was noted for each concentration of propylenediamine in both the series indicating mixed ligand complex formation between Cd^{++} ion on the one hand and propylenediamine and alanine on the other [Table 3.02 and 3.14]. Two sets of F_{ij} [X,Y] obtained from experimental values yield two sets of values of A, B, C and D as depicted in fig. 3.37.

[ala]	log A	log B	log C	log D
0.02 M	3.90	7.04	10.04	12.38

0.04 M 4.00 7.38 10.47 12.48

The three mixed ligand complexes formed had the following composition and stability

$$[\text{Cd (pn) (ala)}]^+ : \log \beta_{11} = 10.16$$

$$[\text{Cd (pn) (ala)}_2] : \log \beta_{12} = 13.17$$

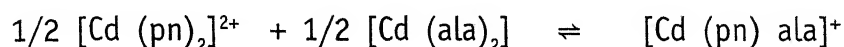
$$[\text{Cd (pn)}_2 \text{ (ala)}]^+ : \log \beta_{21} = 13.65$$

These results broken up into various equilibria are represented in flow sheet diagram 3.07. The numerical figures stand for the logarithm values of equilibria involved.

The equation

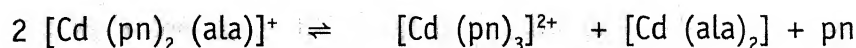
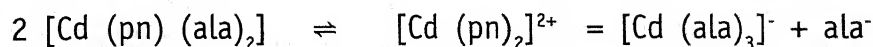
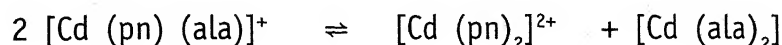
$$\log K_M = \log \beta_{11} + 1/2 (\log \beta_{20} + \log \beta_{02})$$

can be used to evaluate the mixing constant K_M of the equilibrium



It has been found to be + 1.56 for the system. A positive value of K_M is indicative of greater stability of the mixed complex $[\text{Cd (pn) (ala)}]^+$ over simple $[\text{Cd (pn)}_2]^{2+}$ and $[\text{Cd (ala)}_2]$ complexes.

For the following disproportionation reactions



the equilibrium constants are - 3.13, - 7.06 and - 7.65 respectively. The large negative values are once again suggestive of greater stability of mixed ligand complexes over simple binary complexes.

(H) Cd (II) - PROPYLENEDIAMINE - DL - VALINE SYSTEM

During the investigation of mixed ligand formation in this system,

the [val.] was kept constant at 0.02 M and 0.04 M respectively while concentration of propylenediamine increases from 0 to 12×10^{-3} M in both the series. The half wave potential values exhibited a greater cathodic shift in presence of valine than that in each case at each (pn). (Table 3.02 and 3.15). It indicated complex formation of Cd (II) with propylenediamine and valine. The computation of values of F_{ij} [X,Y] functions at the two concentrations of valine (table 3.15) lead to the calculation of the constants A, B, C and D as shown in fig. 3.38.

[val]	log A	log B	log C	log D
0.02 M	4.07	6.95	10.00	12.32
0.04 M	4.07	7.00	10.04	12.28

The two mixed ligand complexes formed had the following composition and stability.

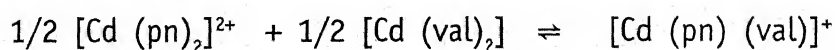


These results broken up into various equilibria are represented in flow sheet diagram 3.08. The numerical figures stand for the logarithm values of equilibria involved.

The equation

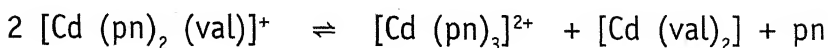
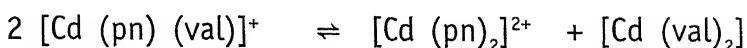
$$\log K_M = \log \beta_{11} - 1/2 (\log) \beta_{20} + \log \beta_{02})$$

can be used to evaluate the mixing constant K_M of the equilibrium



It has been found to be + 1.77 for the system. A positive value of K_M is indicative of greater stability of the mixed complex $[\text{Cd (pn) (val)}]^+$ over simple $[\text{Cd (pn)}_2]^{2+}$ and $[\text{Cd (val)}_2]$ complexes.

For the following disproportionation reactions.



the equilibrium constants are - 3.54 and - 5.06 respectively. The large negative values are once again suggestive of greater stability of mixed ligand complexes over simple binary complexes.

(I) Cd (II) - PROPYLENEDIAMINE - L - ISOLEUCINE SYSTEM

During the investigation of mixed ligand formation in this system, the [isolc] was kept constant at 0.01 M and 0.02 M respectively while concentration of propylenediamine increased from 0 to 12×10^{-3} M in both the series. The half wave potential values exhibited a greater cathodic shift in presence of isoleucine than that in its absence in each case at each [pn] (Table 3.02 and 3.16). It indicated complex formation of Cd (II) with propylenediamine and isoleucine. The F_{ij} [X,Y] functions at the two concentrations of Isoleucine (Table 3.16) lead to the calculation of the constants A, B, C and D. (Fig. 3.39)

[isolc]	log A	log B	log C	log D
0.01 M	3.90	7.07	10.30	12.40
0.02 M	4.07	7.25	10.36	12.47

The two mixed ligand complexes formed had the following composition and stability.



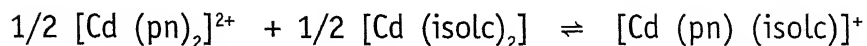
These results broken up into various equilibria are represented in flowsheet diagram 3.09. The numerical figures stand for the logarithm

values of equilibria involved.

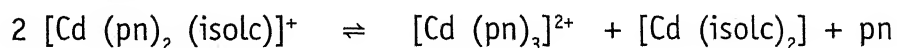
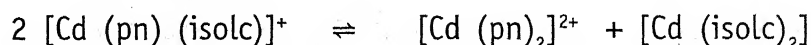
The equation

$$\log K_M = \log \beta_{11} - 1/2 (\log \beta_{20} + 1/2 \beta_{02})$$

can be used to evaluate the mixing constant K_M of the equilibrium



It has been found to be + 2.28 for the system. A positive value of K_M is indicative of greater stability of the mixed complex $[\text{Cd (pn) (isolc)}]^+$ over simple $[\text{Cd (pn)}_2]^{2+}$ and $[\text{Cd (isolc)}_2]$ for the following disproportionation reaction



The equilibrium constants are - 4.56 and - 6.6 respectively. The large negative values are once again suggestive of greater stability of mixed ligand complexes over simple binary complexes.

(J) Cd (II) - PROPYLENEDIAMINE - L - TRYPTOPHAN SYSTEM

During the investigation of mixed ligand formation in this system, the [try] was kept constant at 0.01 M and 0.04 M respectively while concentration of propylenediamine increases from 0 to 12×10^{-3} M in both the series. The half wave potential value exhibited a greater cathodic shift in presence of tryptophan than that in its absence in each case at each (pn) (Table 3.02 and 3.17). It indicated complex formation of Cd (II) with propylenediamine and tryptophan. The computation of F_{ij} [X,Y] functions at the two concentrations of tryptophan (Table 3.17) lead to the calculation of the constants A, B, C and D as illustrated in figure 3.40.

[try]	log A	log B	log C	log D
0.01 M	3.77	7.07	10.32	12.36
0.02 M	3.90	7.30	10.55	12.37

The two mixed ligand complexes formed had the following composition and stability

$$[\text{Cd (pn) (try)}]^+ : \log \beta_{11} = 10.21$$

$$[\text{Cd (pn)}_2 \text{ (try)}]^+ : \log \beta_{21} = 13.39$$

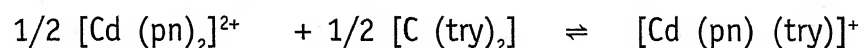
These results broken up into various equilibria are represented in folowsheet diagram 3.10.

The numerical figures stand for the logarithm values of equilibria involved.

The equation

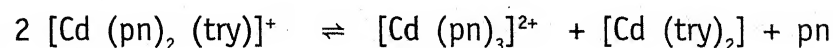
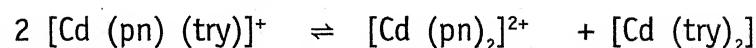
$$\log K_M = \log \beta_{11} - 1/2 (\log \beta_{20} + \log \beta_{02})$$

can be used to evaluate the mixing constant K_M of equilibrium



It has been found be + 0.88 for the system. A positive values of K_M is indicative of greater stability of the mixed complex $[\text{Cd (pn) (try)}]^+$ over simple $[\text{Cd (pn)}_2]^{2+}$ and $[\text{Cd (try)}_2]$ complexes.

For the following disproportionation reaction



The equilibrium constants are - 1.76 and - 5.66 respectively. The large negative values are once again suggestive of greater stability of mixed complexes over simple binary complexes.

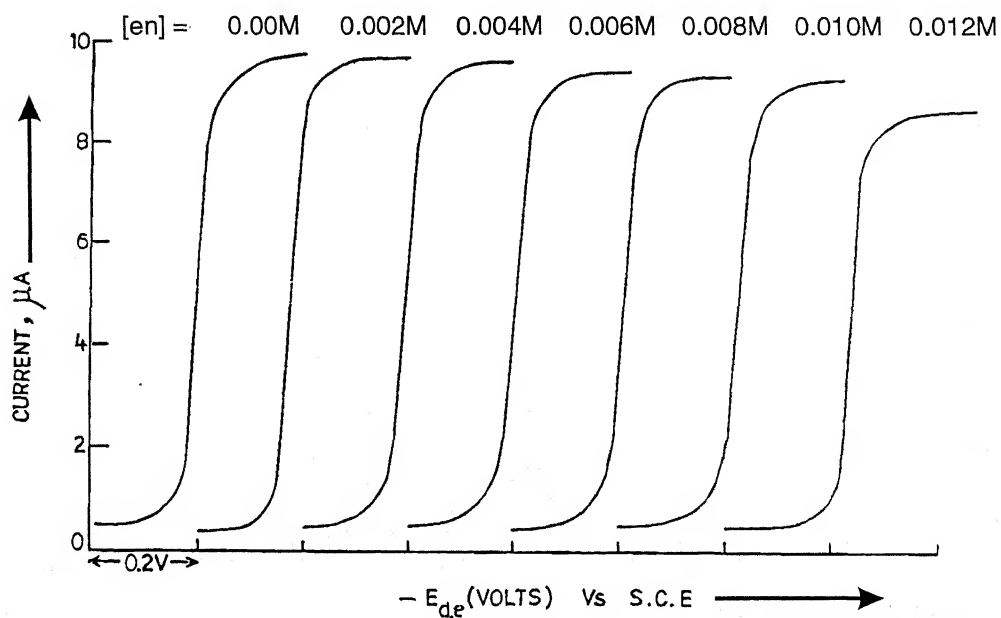


FIG. 3.01 POLAROGRAPHIC WAVES OF Cd(II) - ETHYLENEDIAMINE SYSTEM

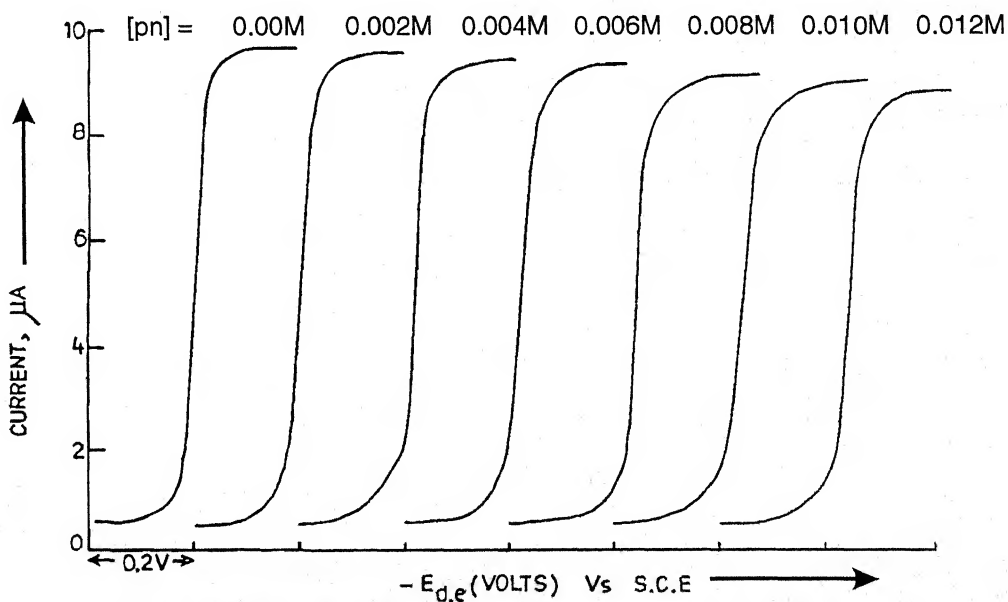


FIG. 3.02 POLAROGRAPHIC WAVES OF Cd(II) - PROPYLENEDIAMINE SYSTEM

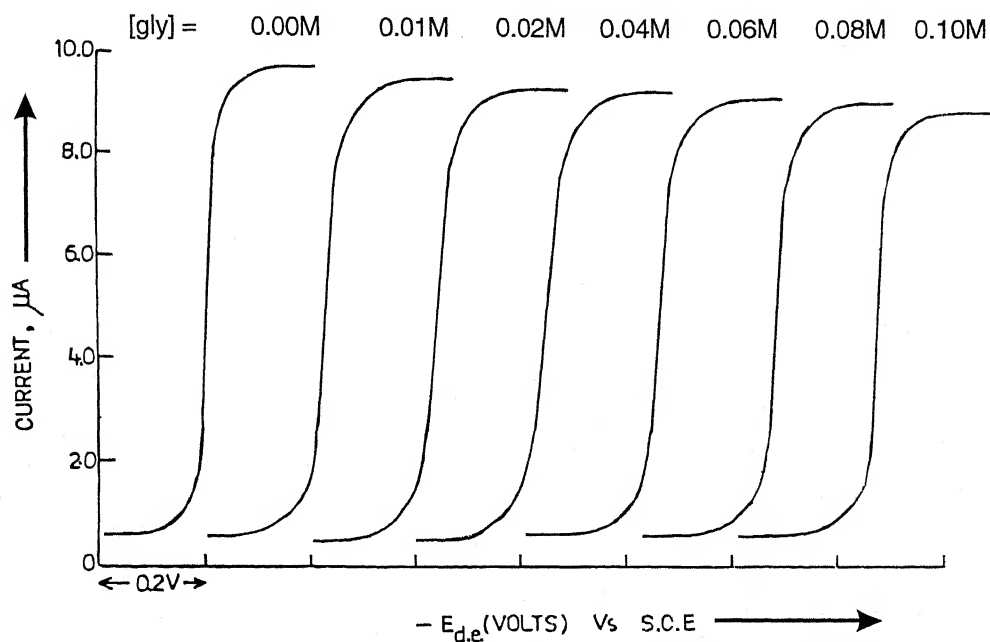


FIG. 3.03 POLAROGRAPHIC WAVES OF Cd(II) - GLYCINE SYSTEM

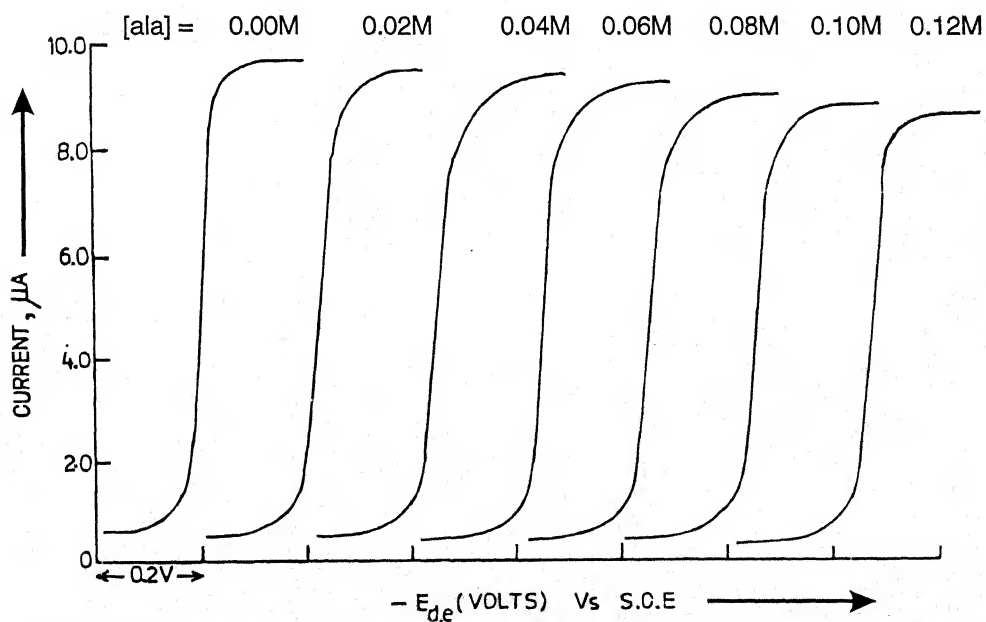


FIG. 3.04 POLAROGRAPHIC WAVES OF Cd(II) - DL - ALANINE SYSTEM

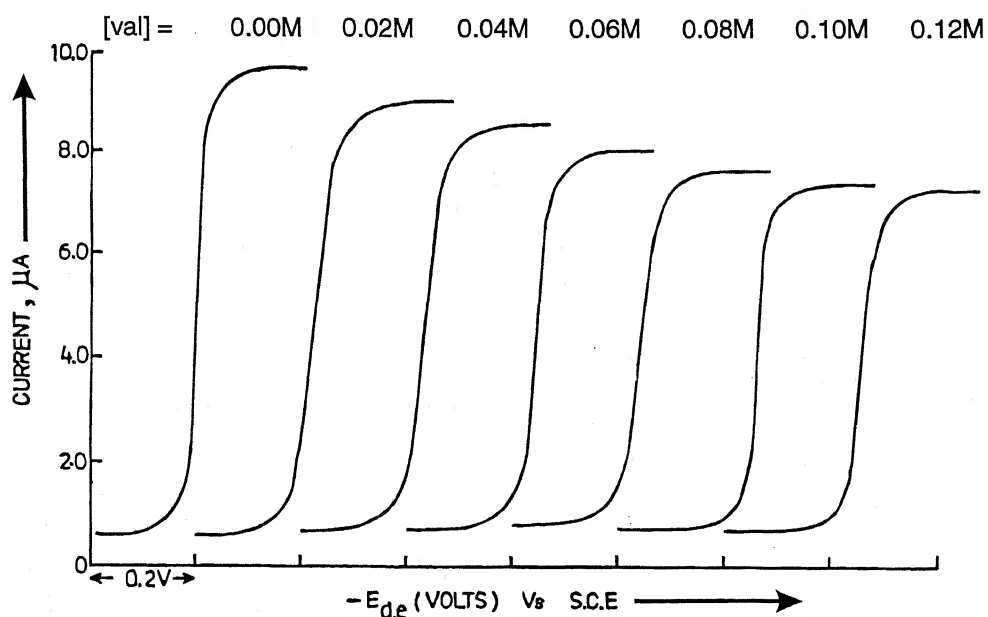


FIG. 3.05 POLAROGRAPHIC WAVES OF Cd(II) - DL - VALINE SYSTEM

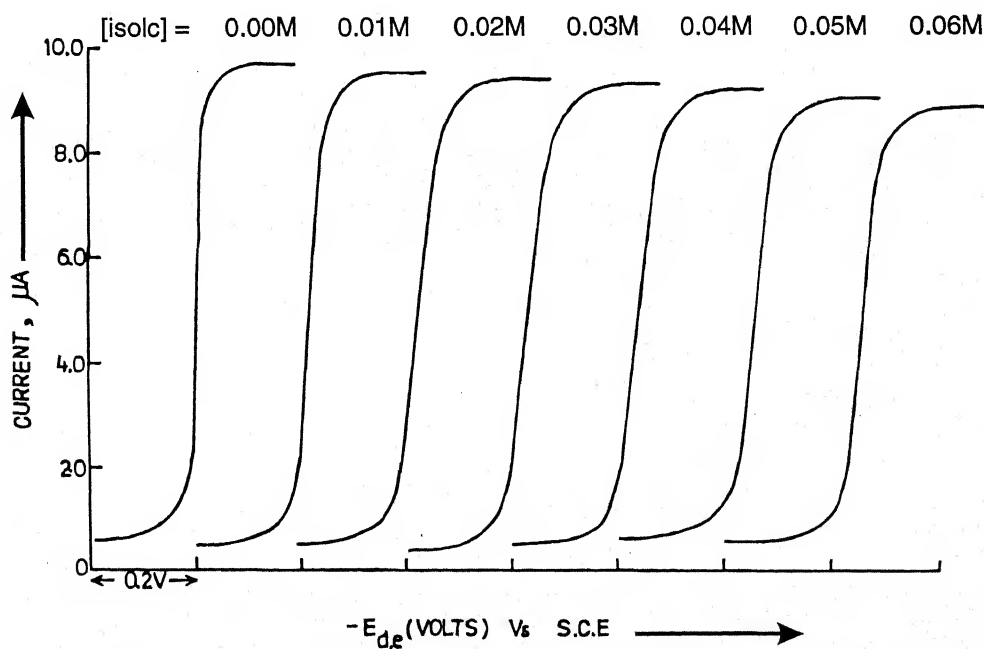


FIG. 3.06 POLAROGRAPHIC WAVES OF Cd(II) - L - ISOLEUCINE SYSTEM

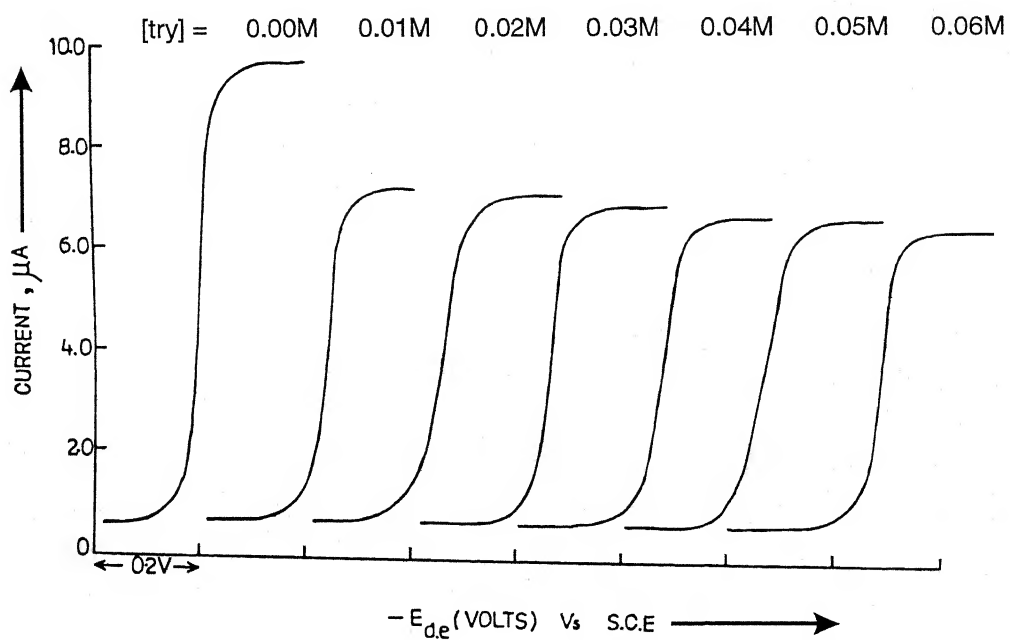


FIG. 3.07 POLAROGRAPHIC WAVES OF Cd(II) - L- TRYPTOPHAN SYSTEM

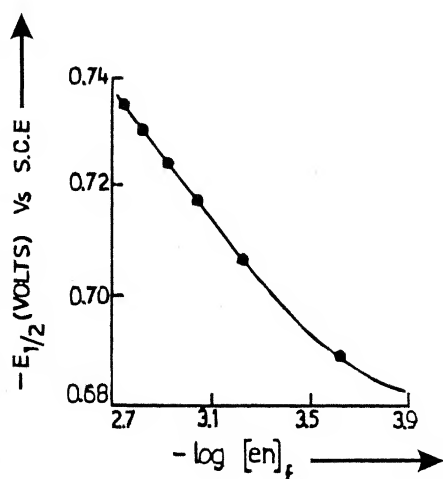


FIG. 3.08 PLOT OF $-E_{1/2}$ Vs $-\log [en]_f$ FOR Cd (II) - ETHYLENEDIAMINE SYSTEM

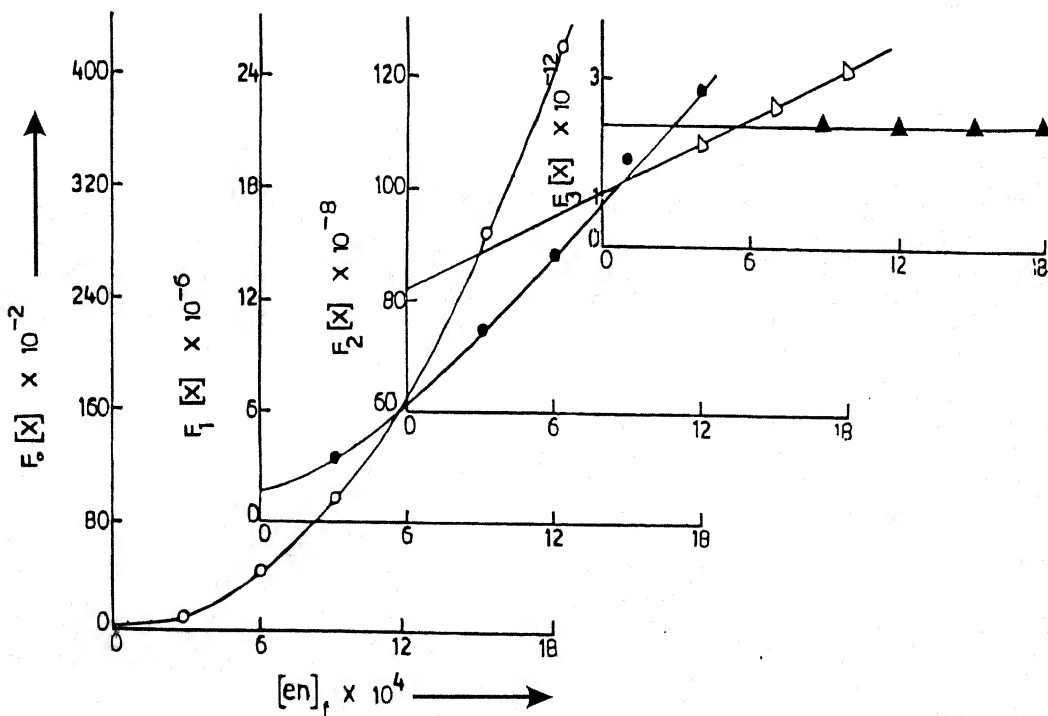


FIG. 3.09 PLOT OF $F_1[X]$ Vs $[en]_f$ FOR Cd (II) - ETHYLENEDIAMINE SYSTEM

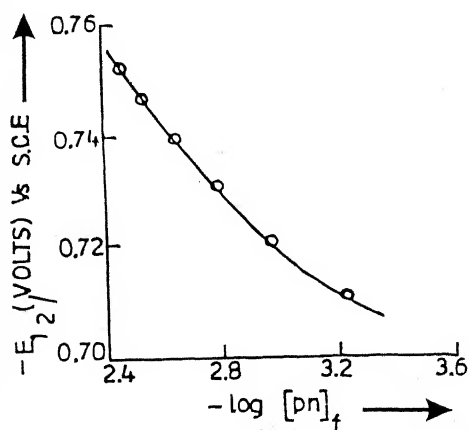


FIG. 3.10 PLOT OF $-E_2$ Vs $-\log [pn]_f$ FOR Cd (II) PROPYLENEDIAMINE SYSTEM

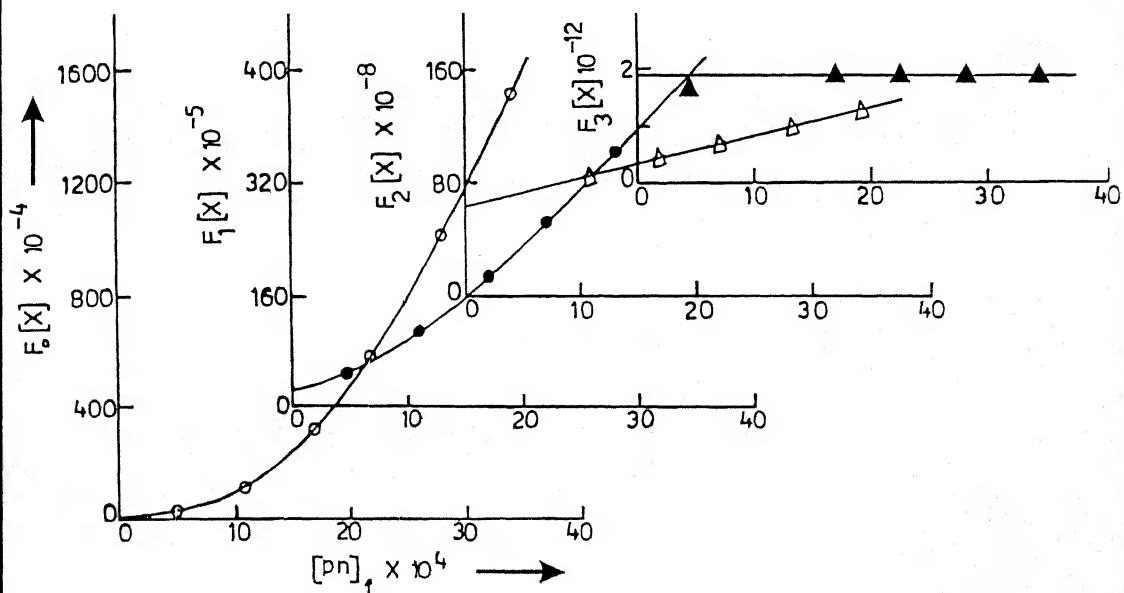


FIG. 3.11 PLOT OF $F_i [X]$ Vs $[pn]_f$ FOR Cd (II) PROPYLENEDIAMINE SYSTEM

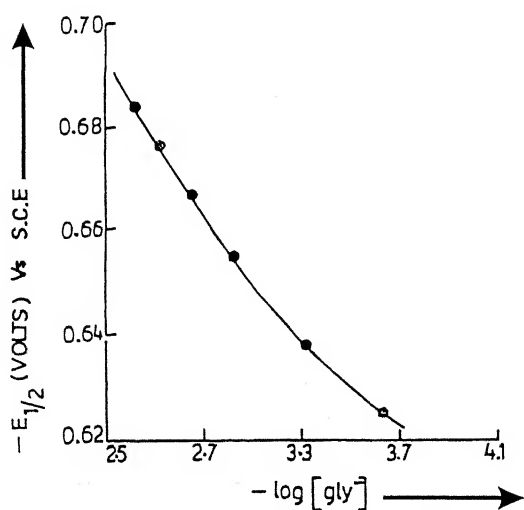


FIG. 3.12 PLOT OF $-E_{1/2}$ Vs $-\log [\text{gly}]$ FOR Cd (II) GLYCINE SYSTEM

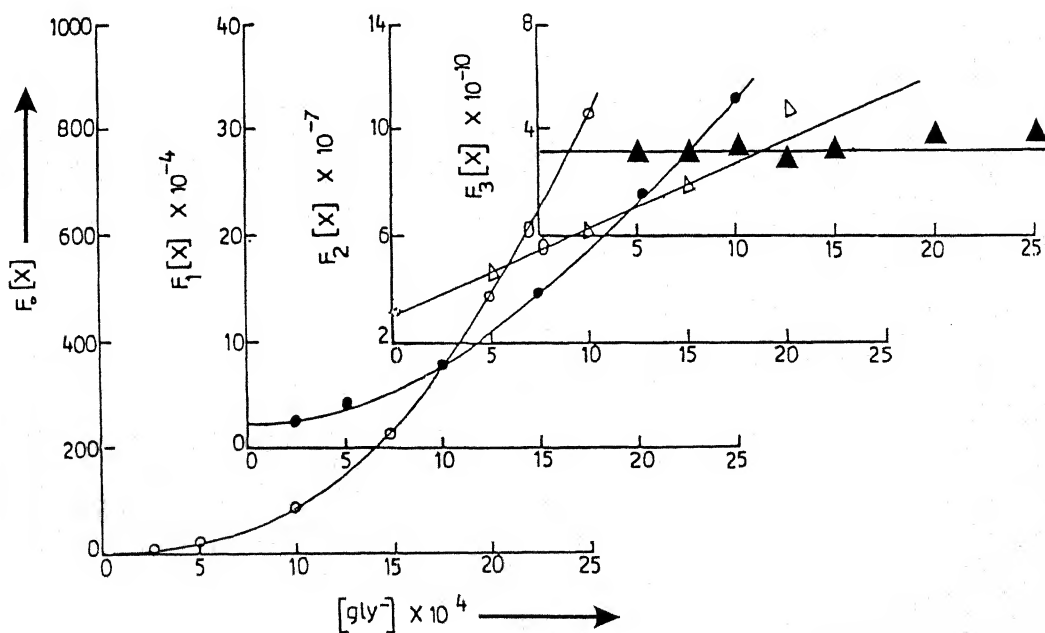


FIG. 3.13 PLOT OF $F_1[X]$ Vs $[\text{gly}]$ FOR Cd (II) - GLYCINE SYSTEM

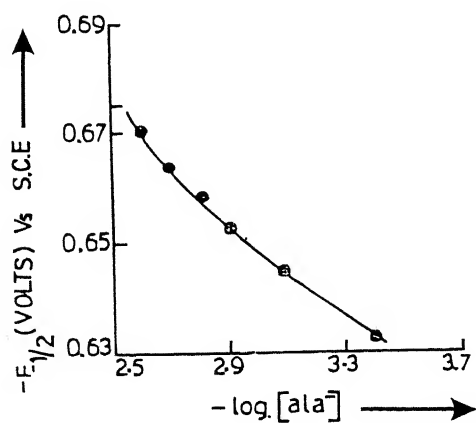


FIG. 3.14 PLOT OF $-E_{1/2}$ Vs $-\log [ala^-]$ FOR Cd (II) - DL - ALANINE SYSTEM

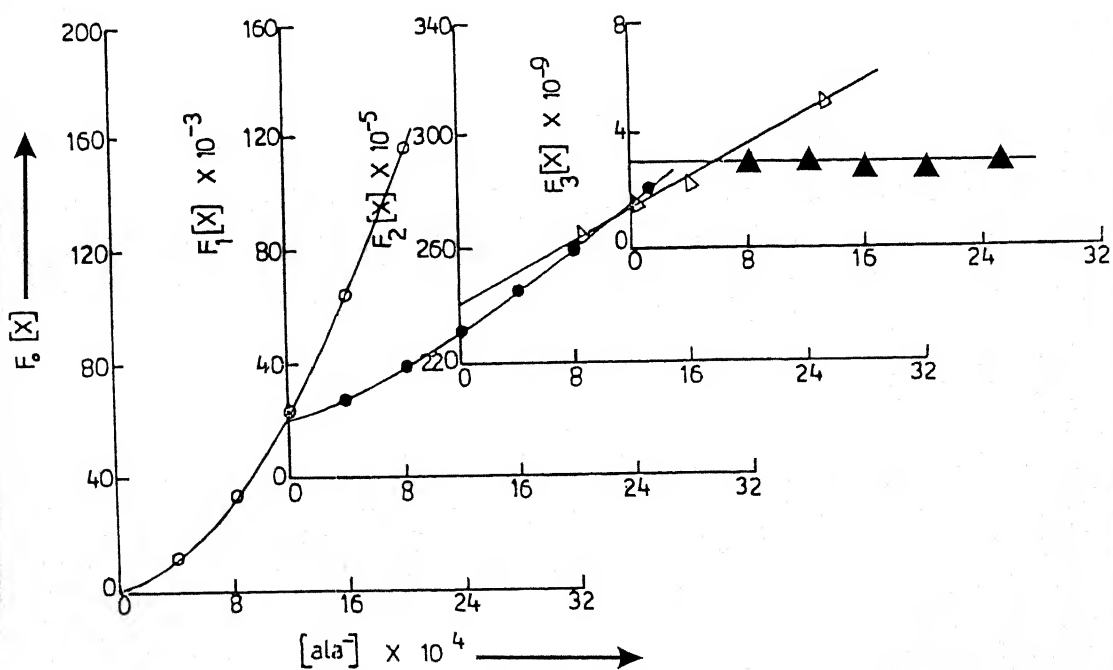


FIG. 3.15 PLOT OF $F_i [X]$ Vs $[ala^-]$ FOR Cd (II) - DL - ALANINE SYSTEM

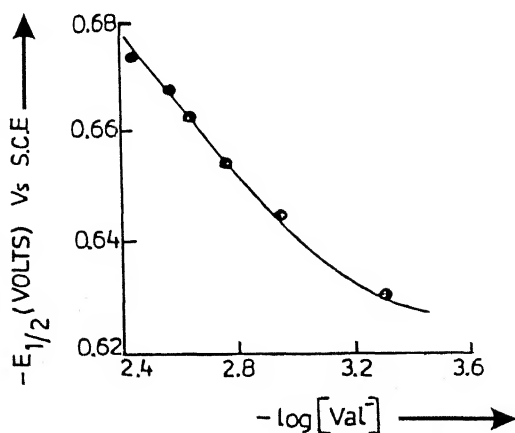


FIG. 3.16 PLOT OF $-E_{1/2}$ Vs $-\log [\text{Val}^+]$ FOR Cd (II) - DL - VALINE SYSTEM

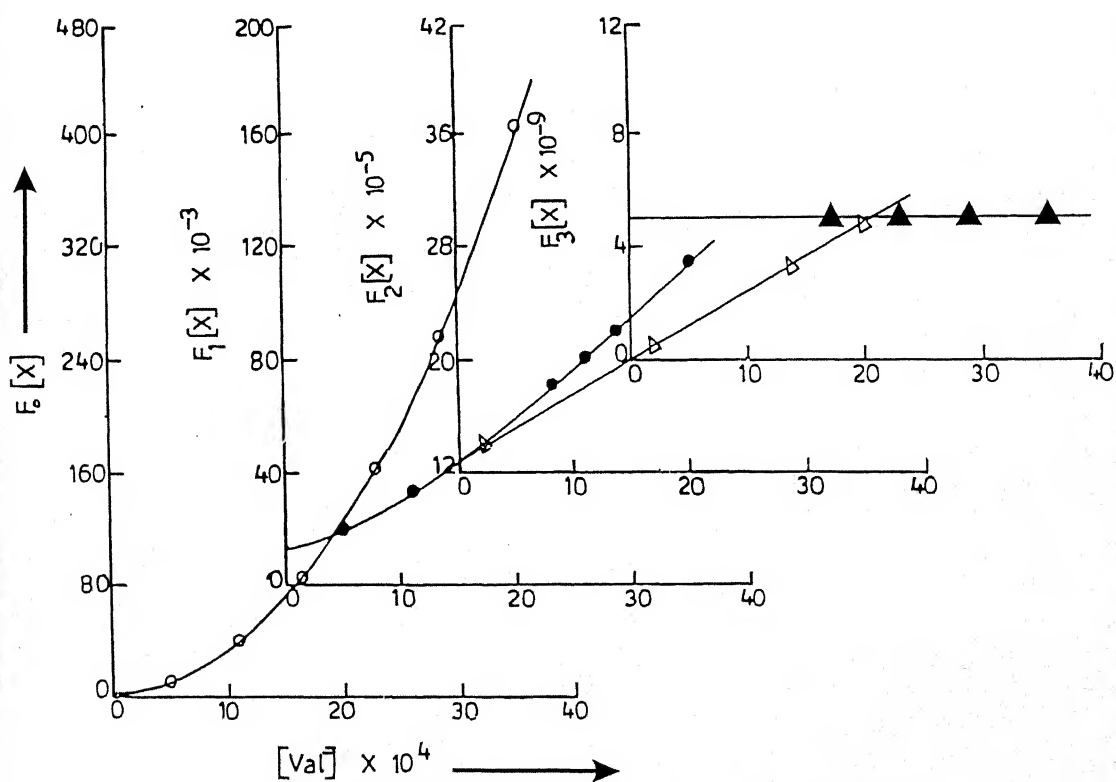


FIG. 3.17 PLOT OF $F_1[X]$ Vs $[\text{Val}^+]$ FOR Cd (II) - DL - VALINE SYSTEM

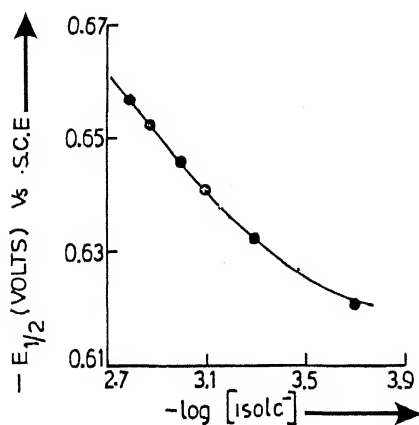


FIG. 3.18 PLOT OF $-E_{1/2}$ Vs $-\log [\text{isolc}^-]$ FOR Cd - L - ISOLEUCINE SYSTEM

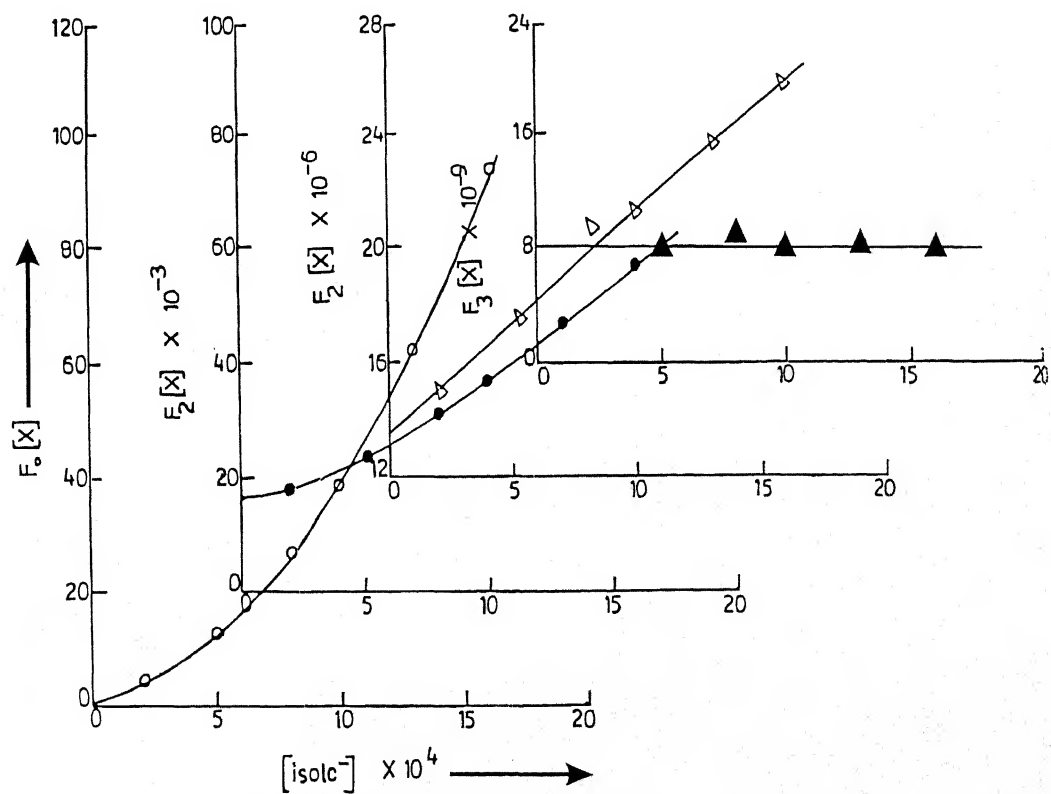


FIG. 3.19 PLOT OF $F_i[X]$ Vs $\log [\text{isolc}^-]$ FOR Cd (II) - L - ISOLEUCINE SYSTEM

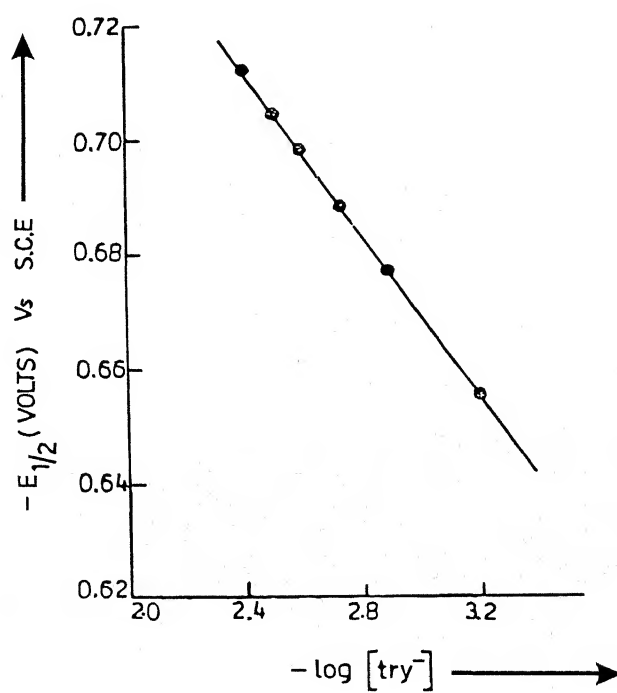


FIG. 3.20 PLOT OF $-E_{1/2}$ Vs $-\log [\text{try}^-]$ FOR Cd (II) - L - TRYPTOPHAN

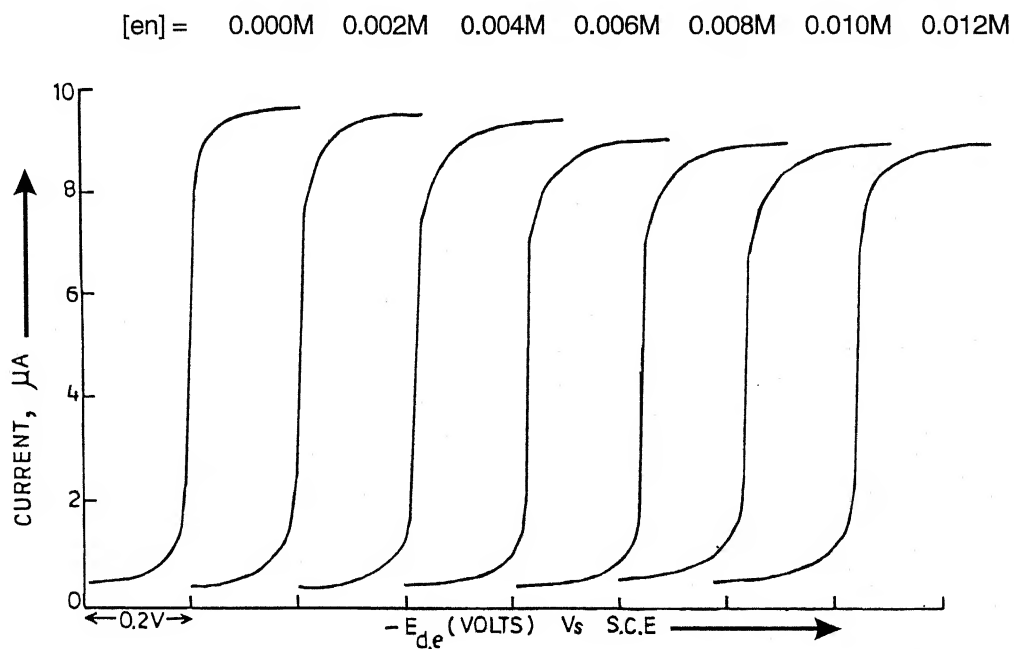
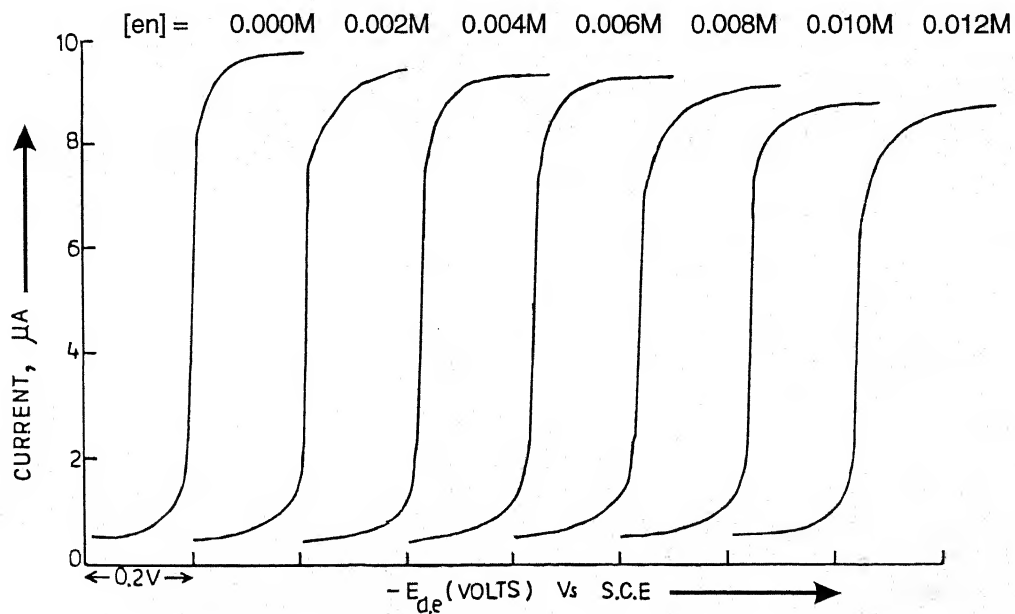
SERIES-I**SERIES-II**

FIG. 3.21 POLAROGRAPHIC WAVES OF Cd(II) - ETHYLENEDIAMENE GLYCINE SYSTEM

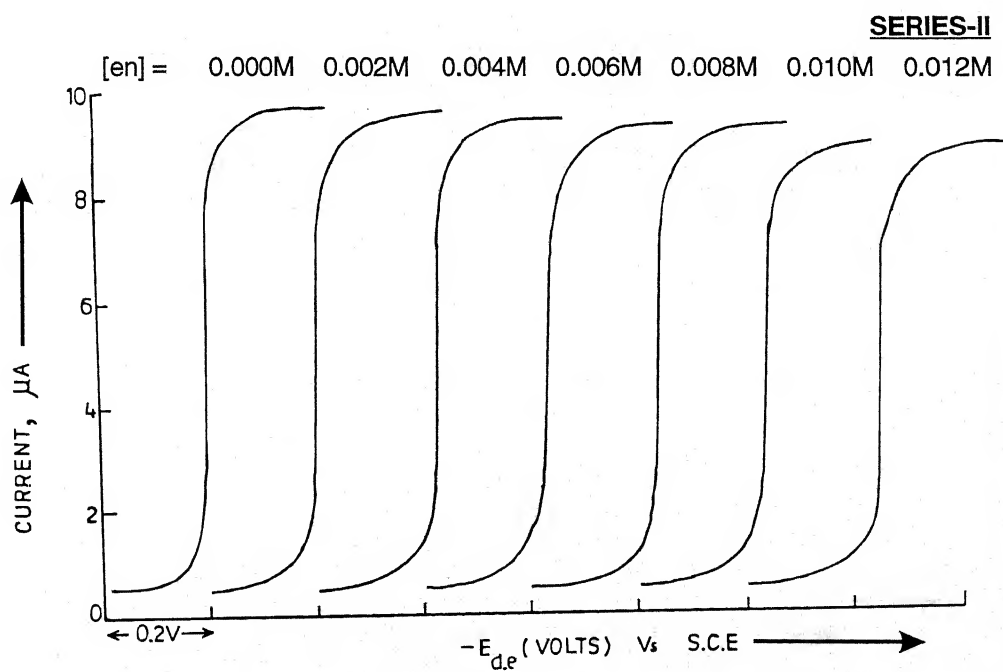
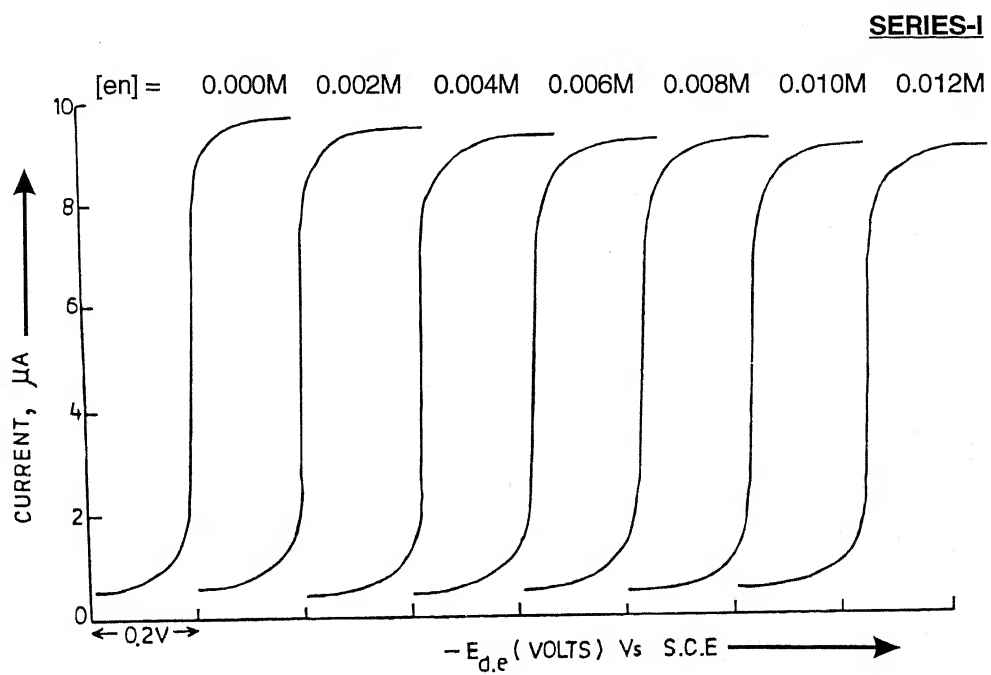


FIG. 3.22 POLAROGRAPHIC WAVES OF Cd(II) - ETHYLENEDIAMINA - DL- ALANINE SYSTEM

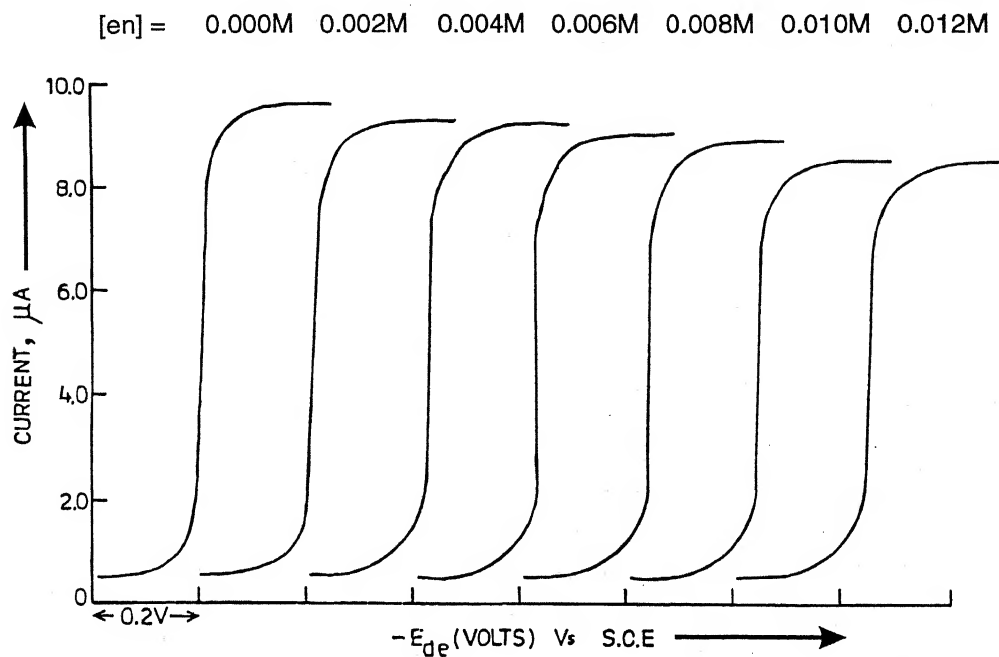
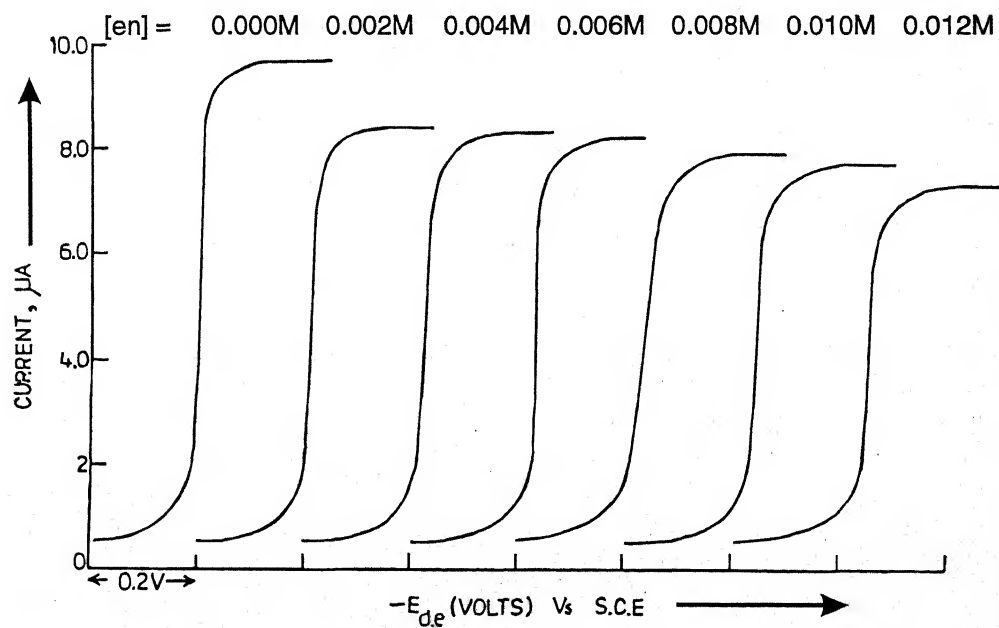
SERIES-I**SERIES-II**

FIG. 3.23 POLAROGRAPHIC WAVES OF Cd(II) - ETHYLENEDIAMINA - DL- VALINE SYSTEM

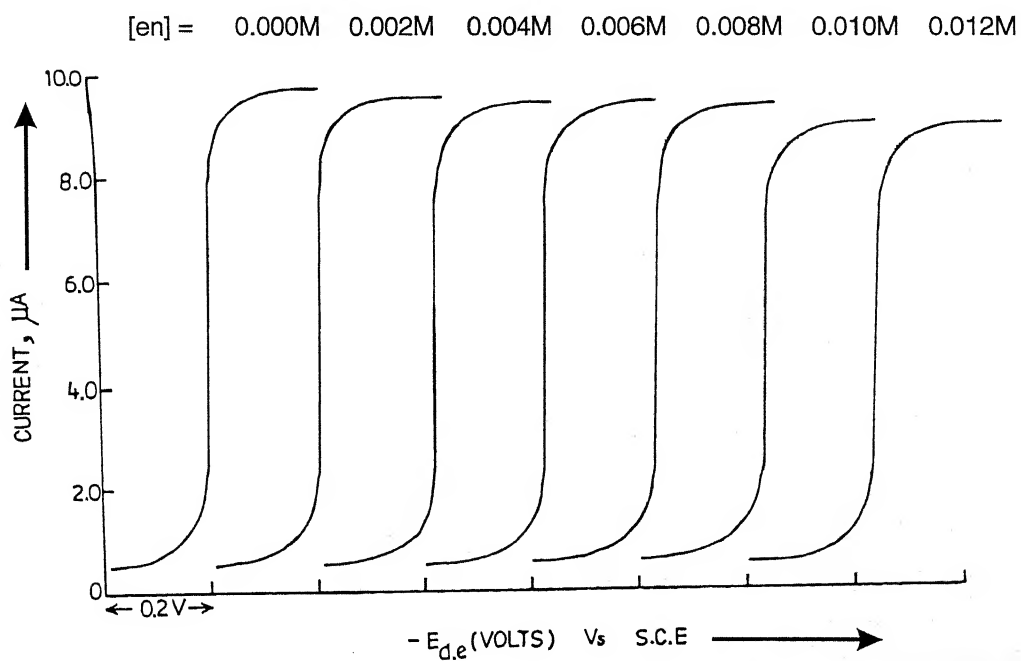
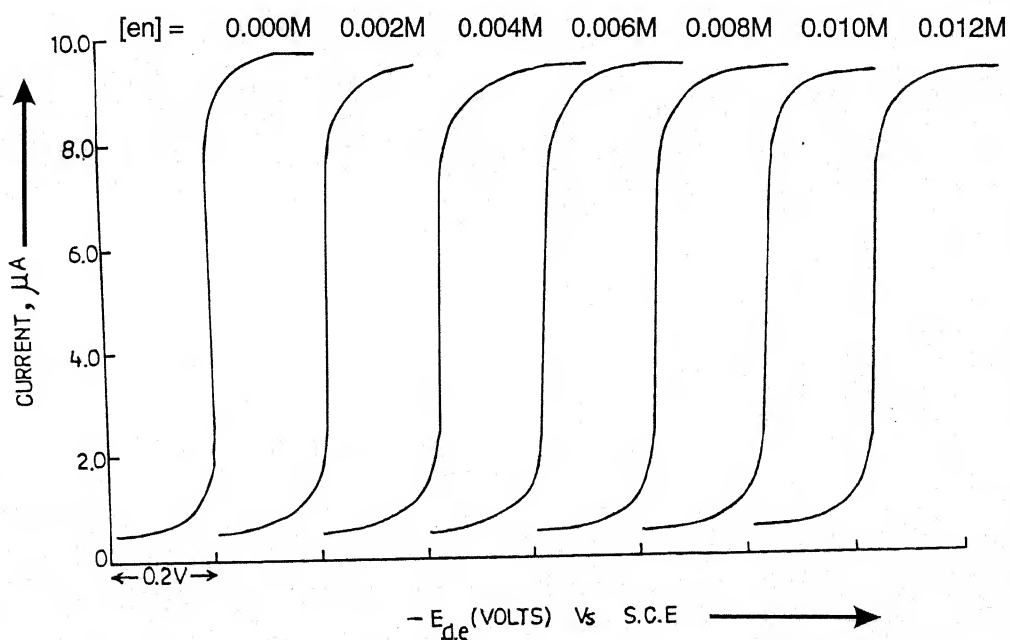
SERIES-I**SERIES-II**

FIG. 3.24 POLAROGRAPHIC WAVES OF Cd(II) - ETHYLENEDIAMINE - L - ISOLEUCINE SYSTEM

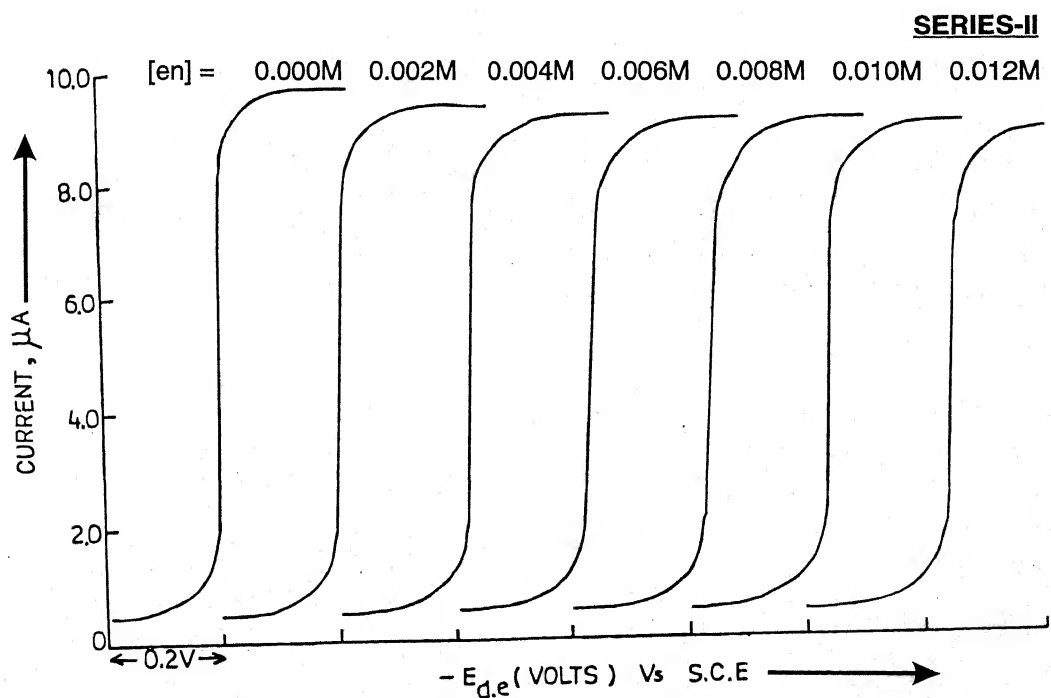
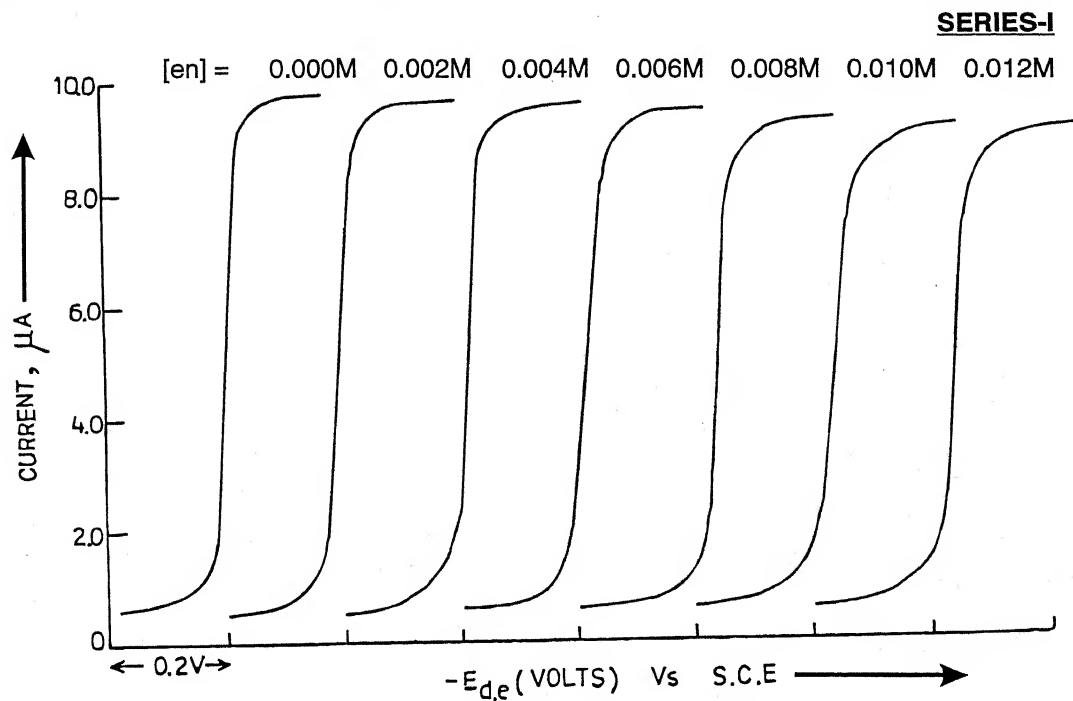
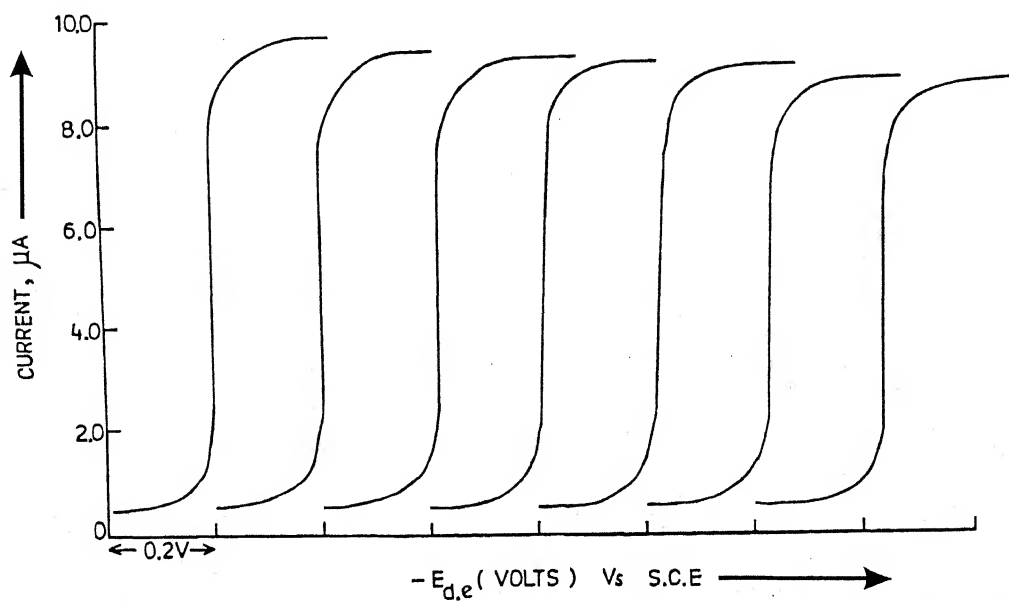


FIG. 3.25 POLAROGRAPHIC WAVES OF Cd(II) - ETHYLENEDIAMINE - L - TRYPTOPHAN SYSTEM

SERIES-I

[pn] = 0.000M 0.002M 0.004M 0.006M 0.008M 0.010M 0.012M

**SERIES-II**

[pn] = 0.000M 0.002M 0.004M 0.006M 0.008M 0.010M 0.012M

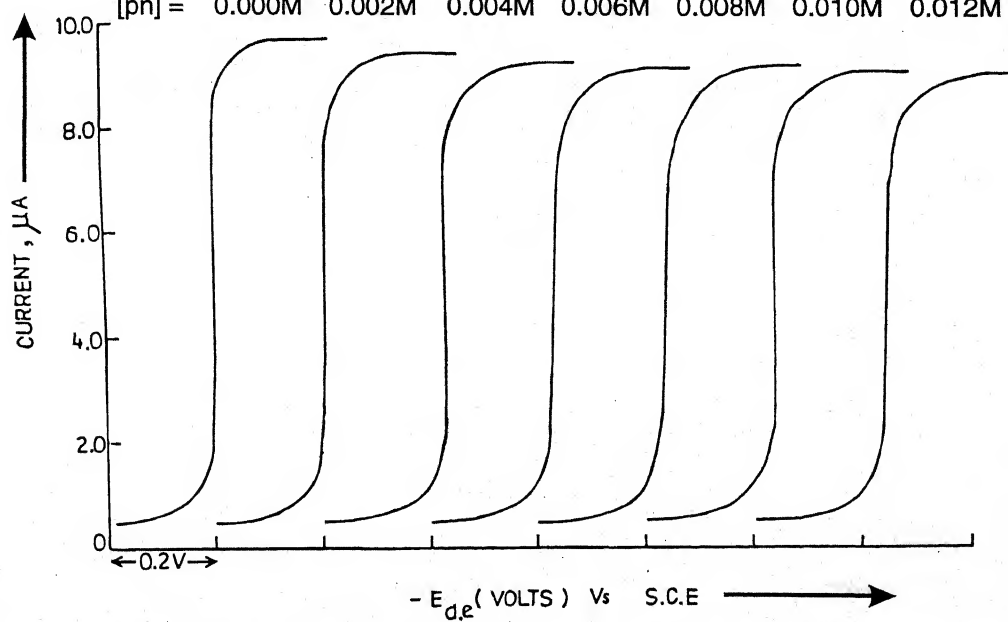


FIG. 3.26 POLAROGRAPHIC WAVES OF Cd(II) - PROPYLENEDIAMINE GLYCINE SYSTEM

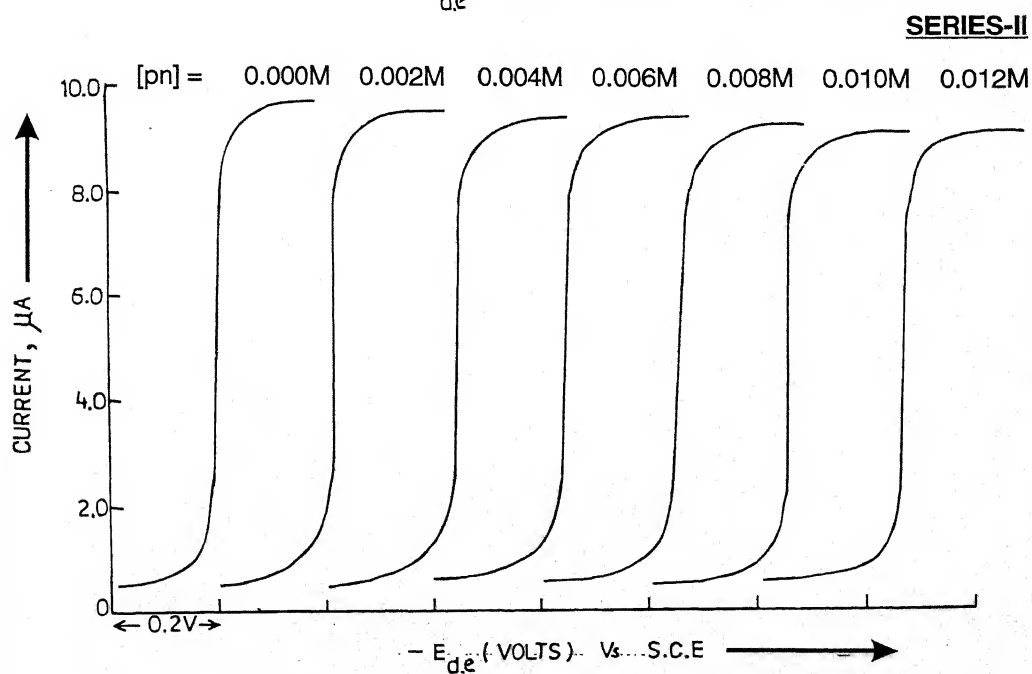
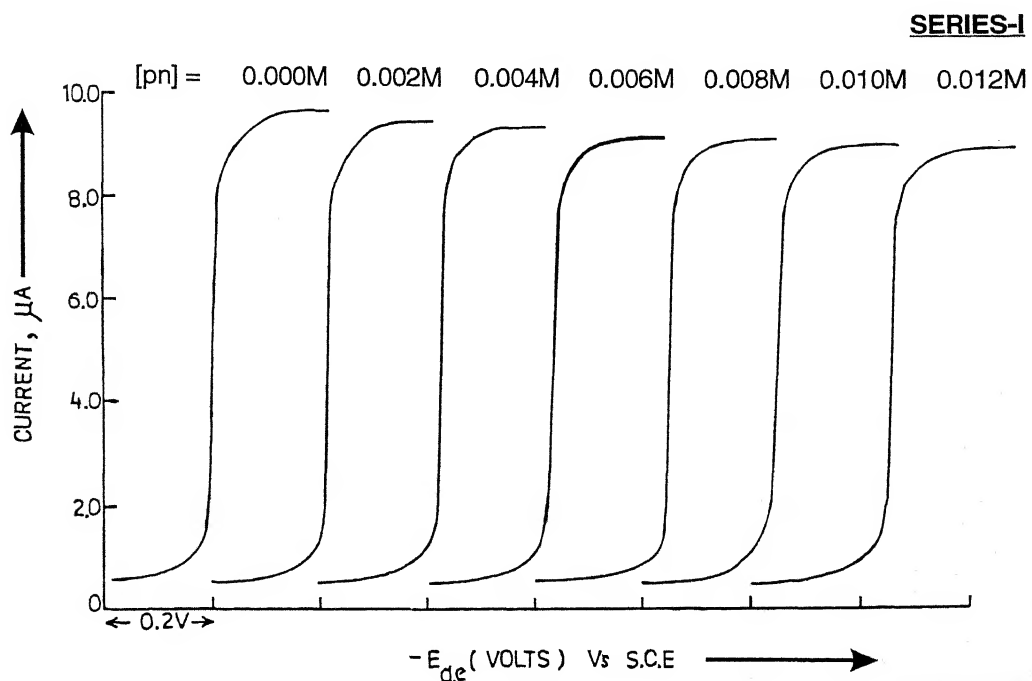


FIG. 3.27 POLAROGRAPHIC WAVES OF Cd(II) - PROPYLENEDIAMINE - DL - ALANINE SYSTEM

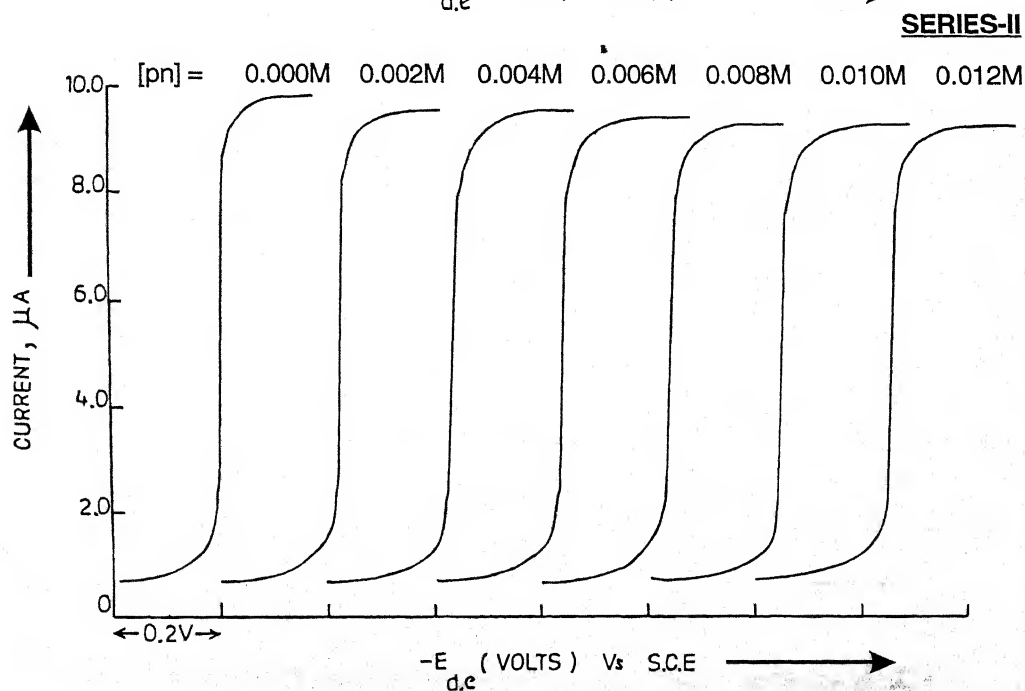
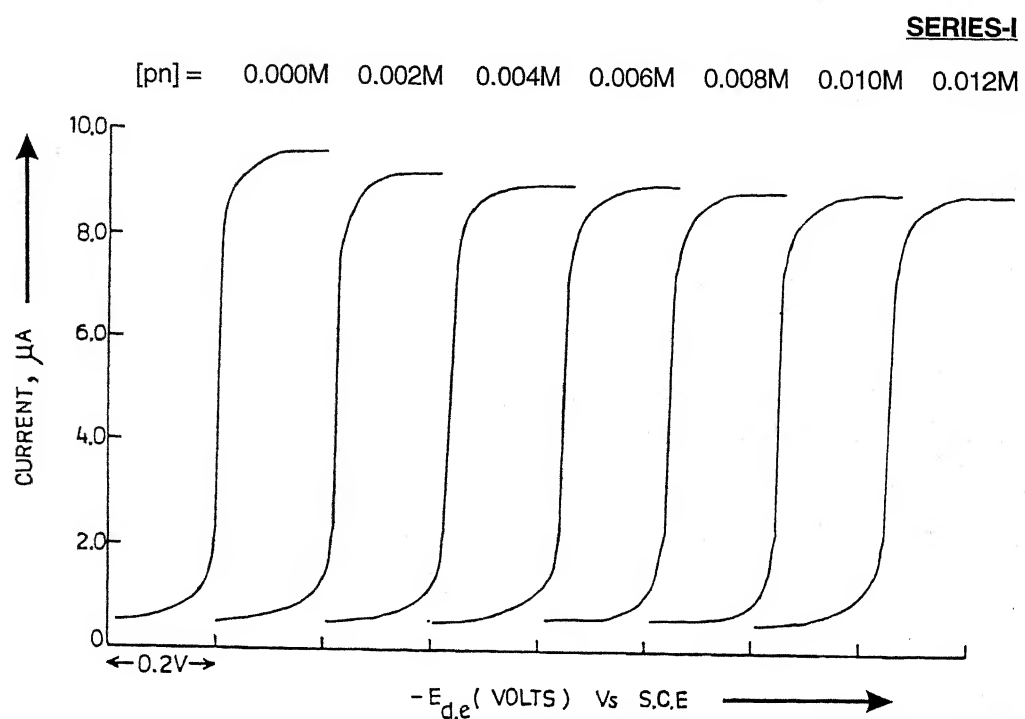


FIG. 3.28 POLAROGRAPHIC WAVES OF Cd(II) - PROPYLENEDIAMINE DL - VALINE SYSTEM

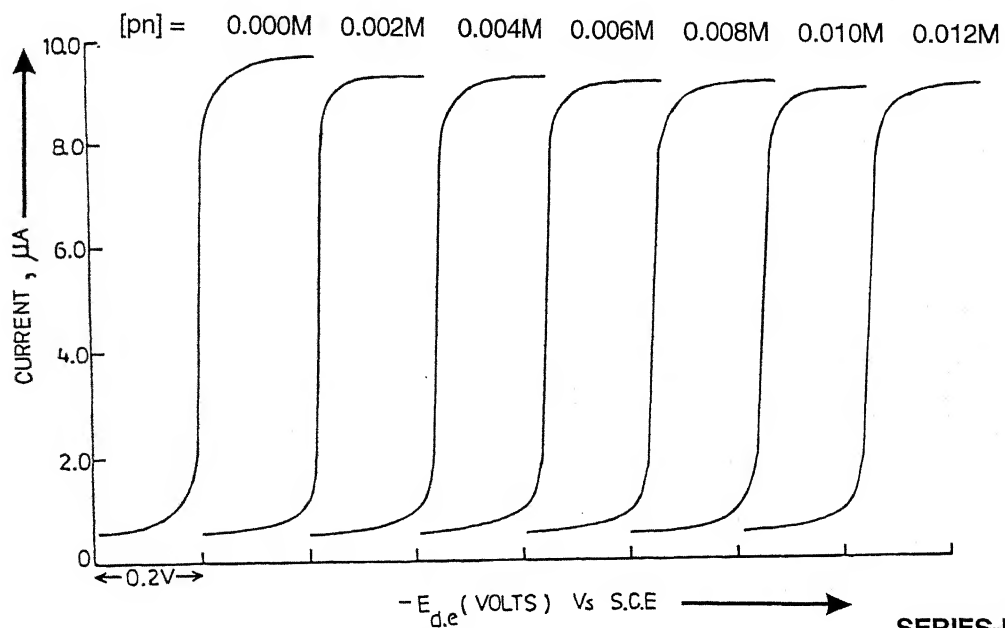
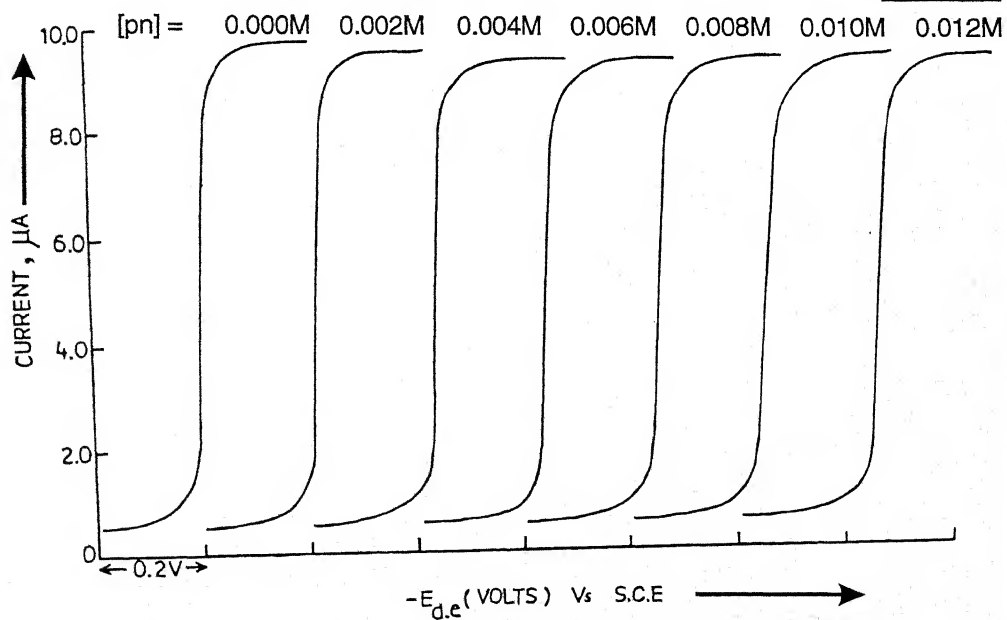
SERIES-I**SERIES-II**

FIG. 3.29 POLAROGRAPHIC WAVES OF Cd(II) - PROPYLENEDIAMINE -L- ISOLUCINE SYSTEM

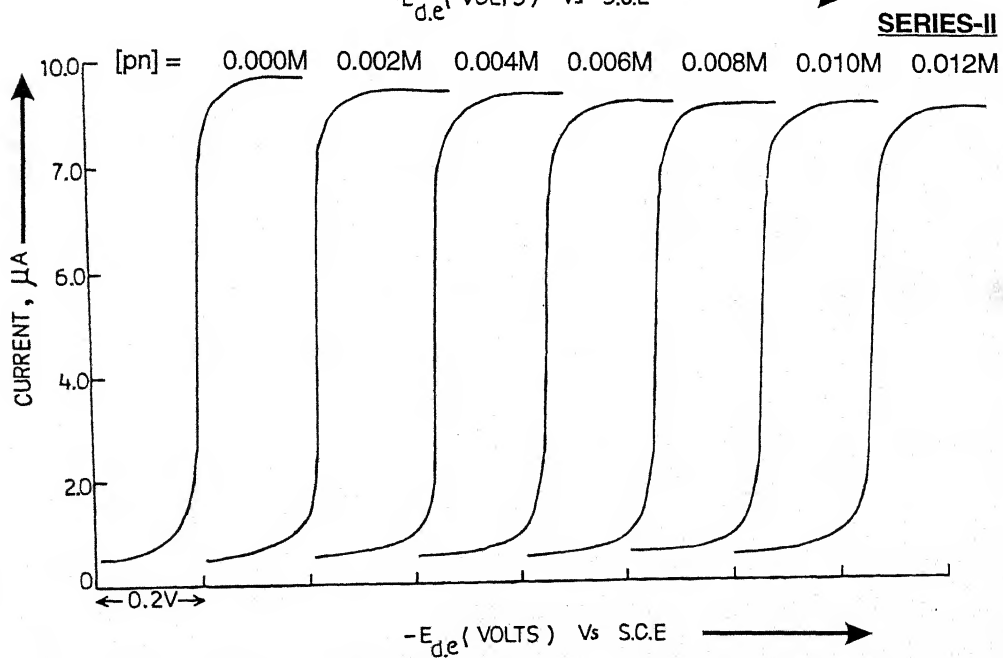
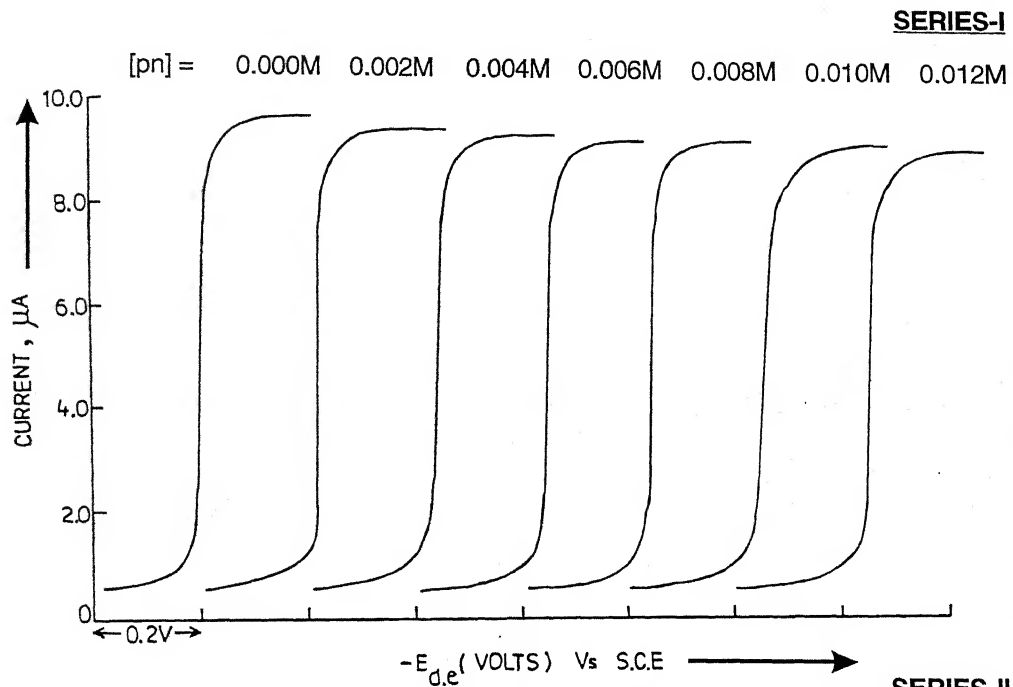


FIG. 3.30 POLAROGRAPHIC WAVES OF Cd(II) - PROPYLENEDIAMINE
- L - TRYPTOPHAN SYSTEM

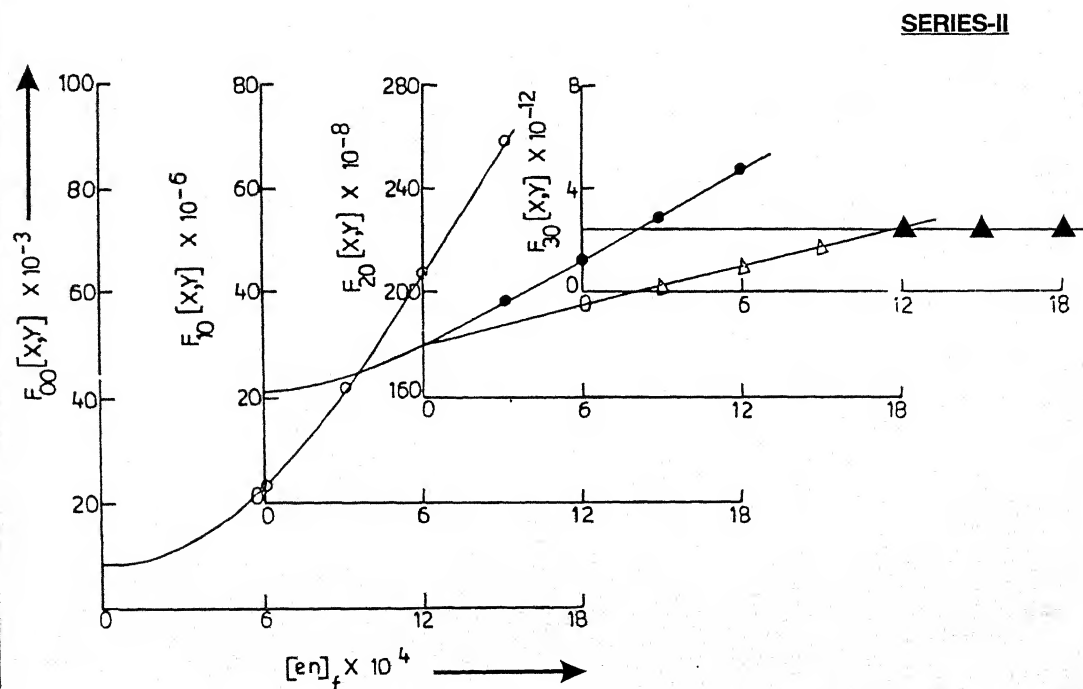
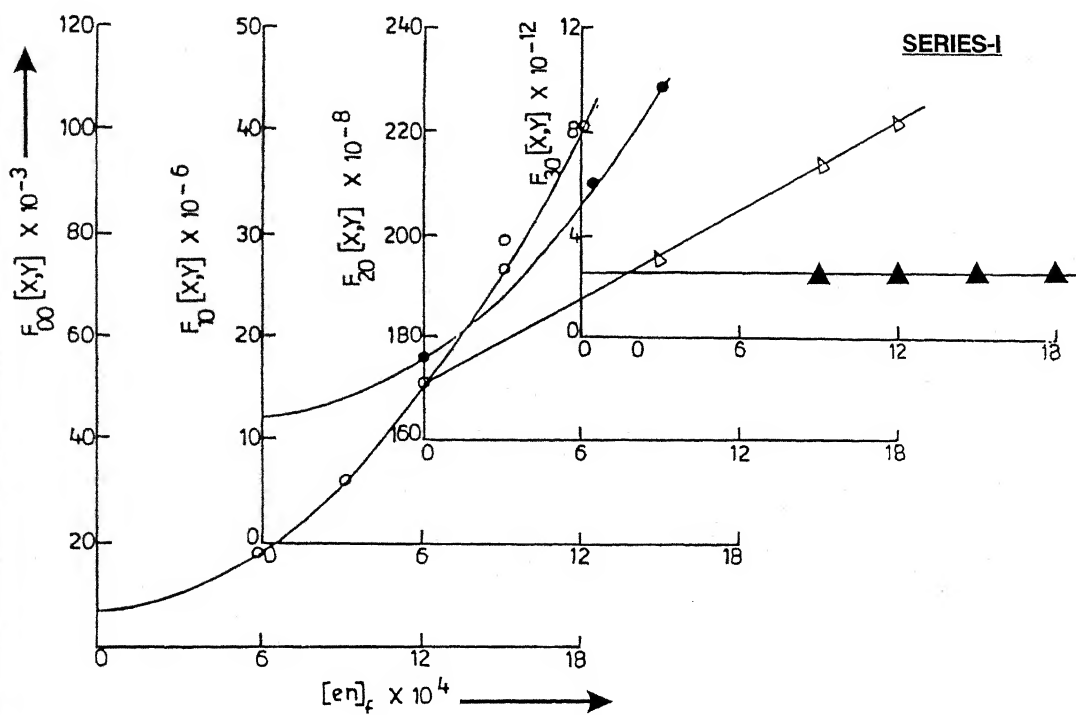


FIG. 3.31 PLOT OF $F_i [X,Y]$ FUNCTIONS FOR Cd (II) - ETHYLENEDIAMINE GLYCINE SYSTEM

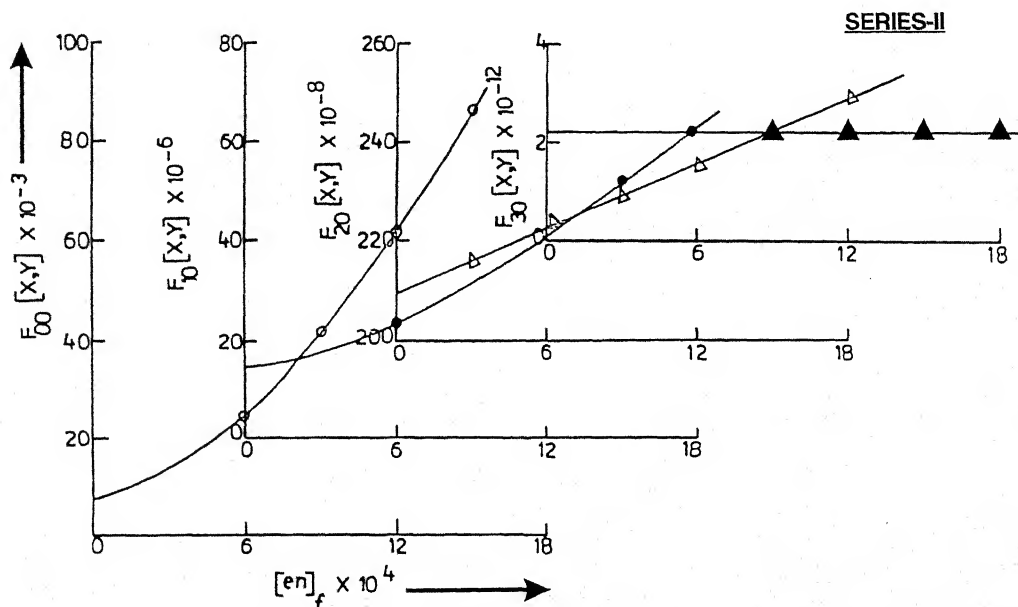
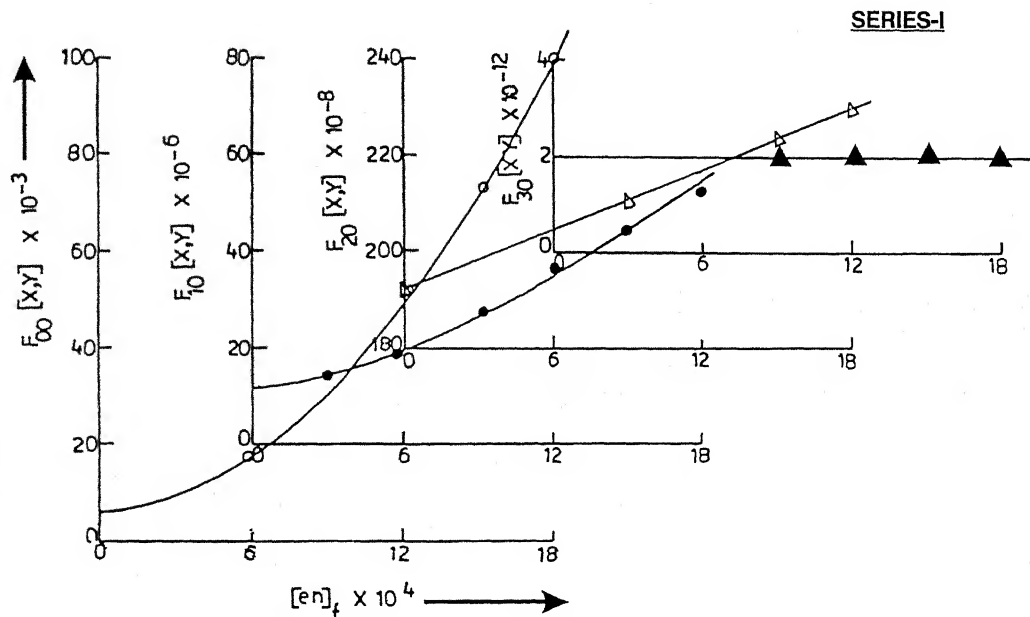


FIG. 3.32 PLOT OF $F_i[X,Y]$ FUNCTIONS FOR Cd (II) - ETHYLENEDIAMINE - DL - ALANINE SYSTEM

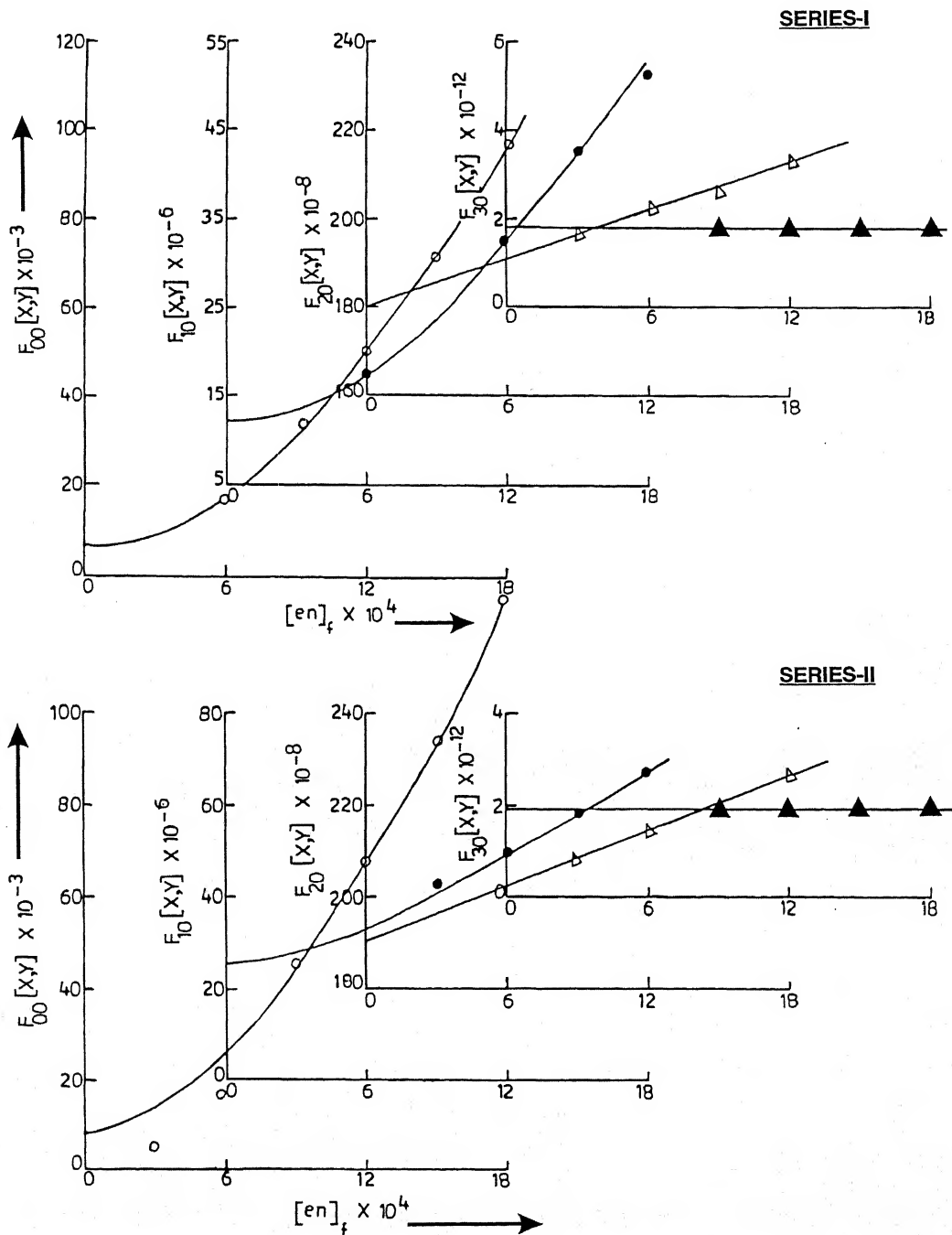


FIG. 3.33 POLT OF $F_i[X,Y]$ FUNCTIONS FOR Cd(II) - ETHYLENEDIAMINE - DL - VALINE SYSTEM

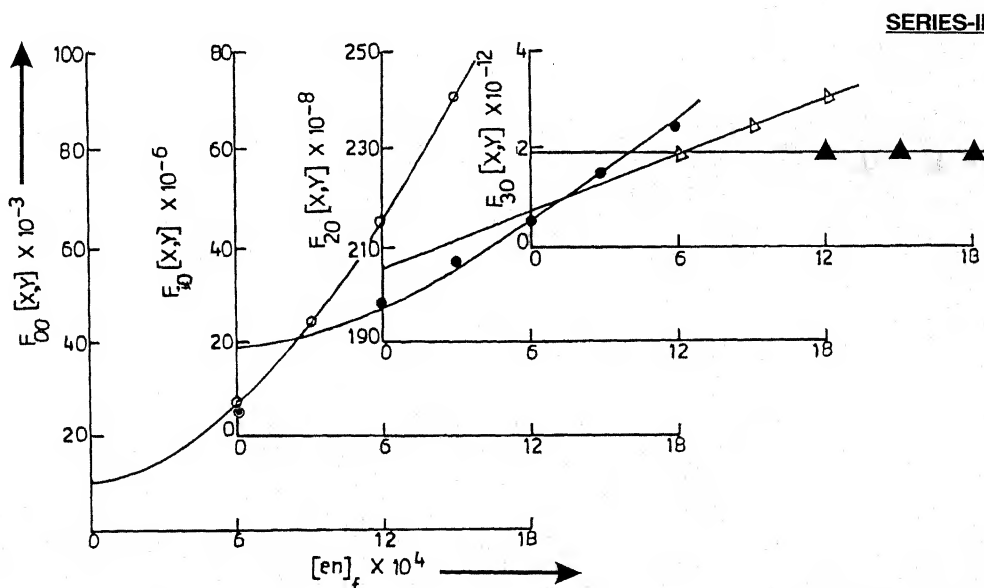
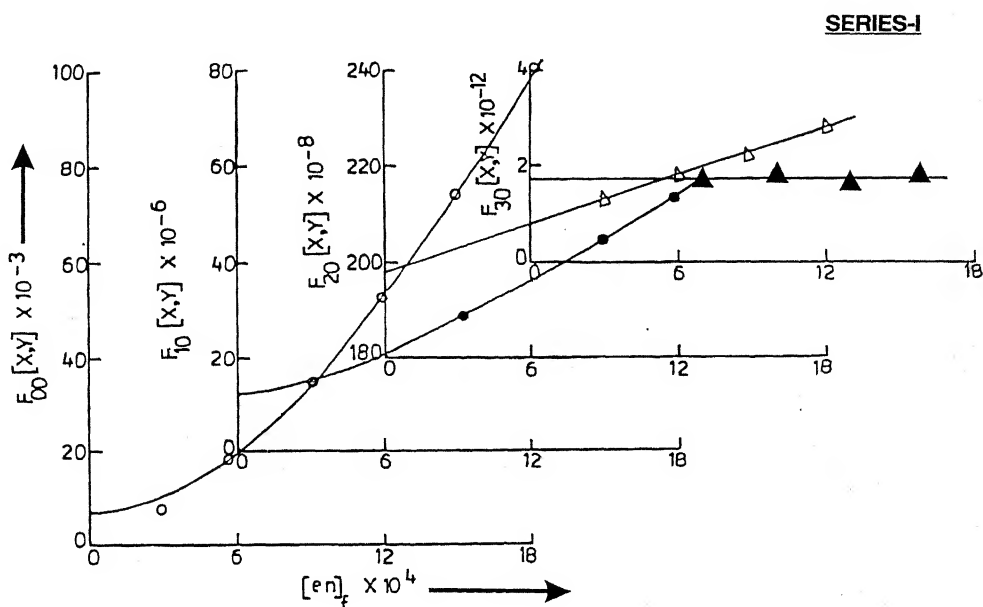


FIG. 3.34 PLOT OF $F_i [X,Y]$ FUNCTIONS FOR Cd (II) - ETHYLENEDIAMINE - L - ISOLEUCINE SYSTEM

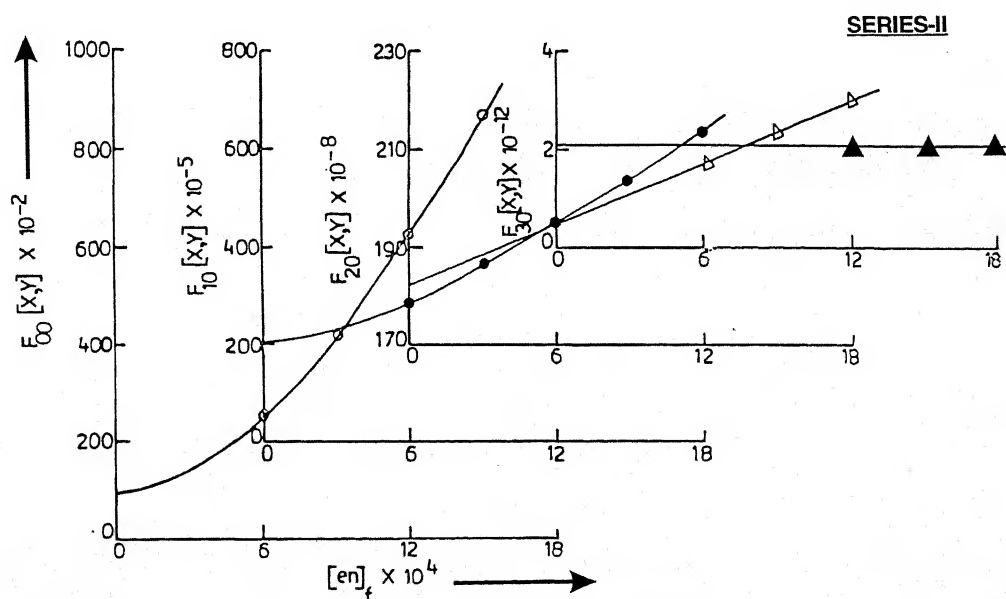
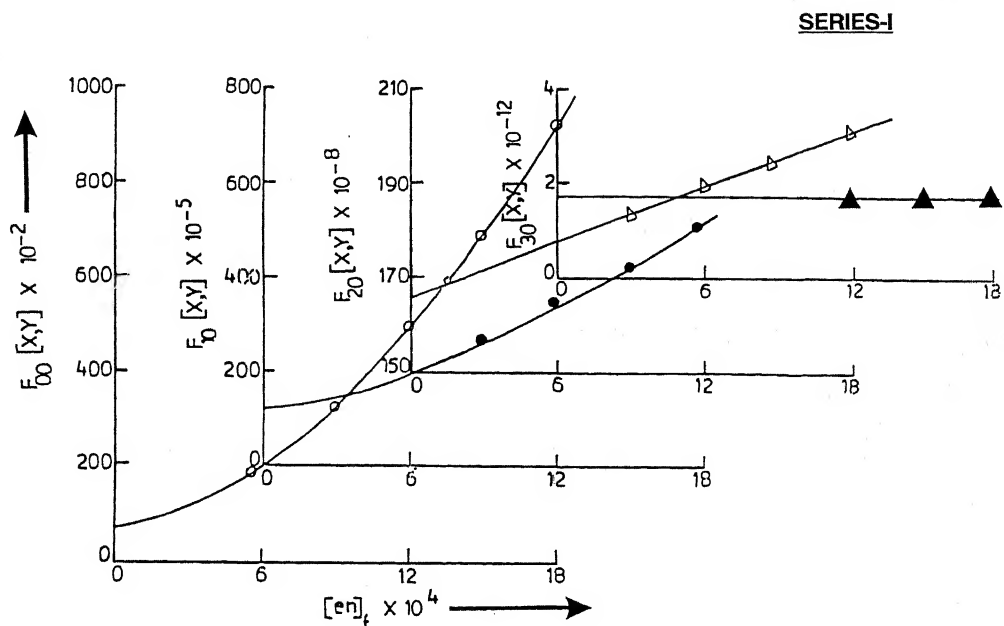


FIG. 3.35 PLOT OF $F_n [X, Y]$ FUNCTIONS FOR Cd (II) - ETHYLENEDIAMINE - L - TRYPTOPHAN SYSTEM

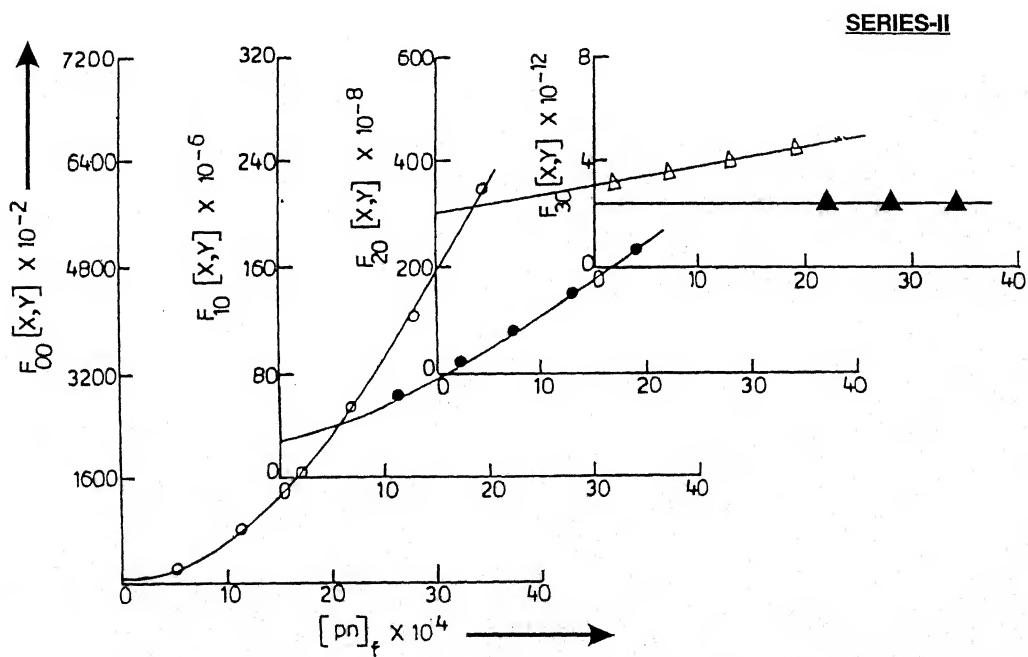
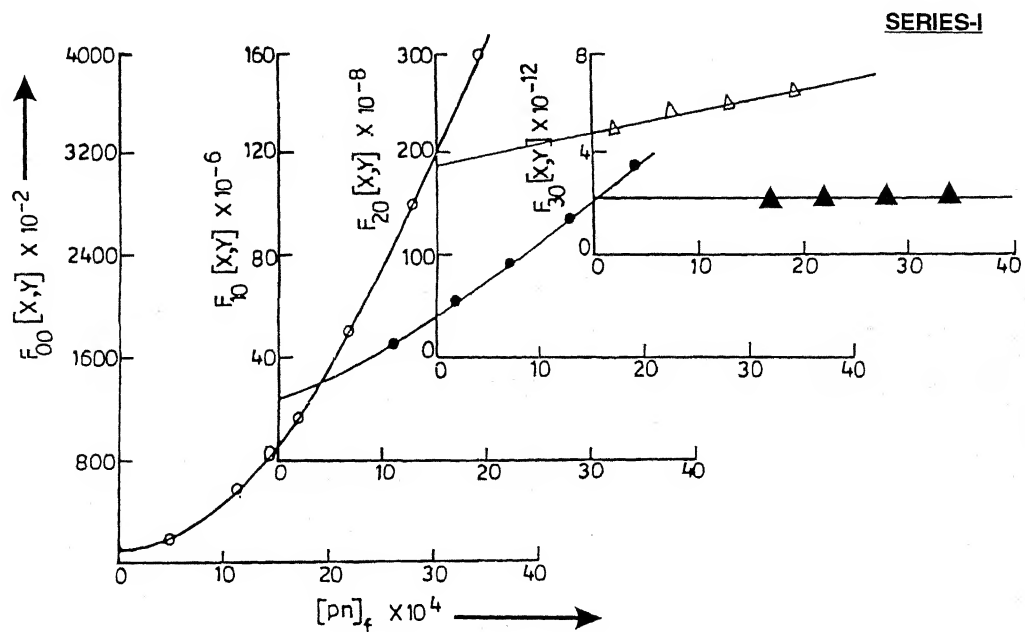


FIG. 3.36 POLT OF $F_i [X,Y]$ FUNCTIONS FOR Cd (II) - PROPYLENEDIAMINE GLYCINE SYSTEM

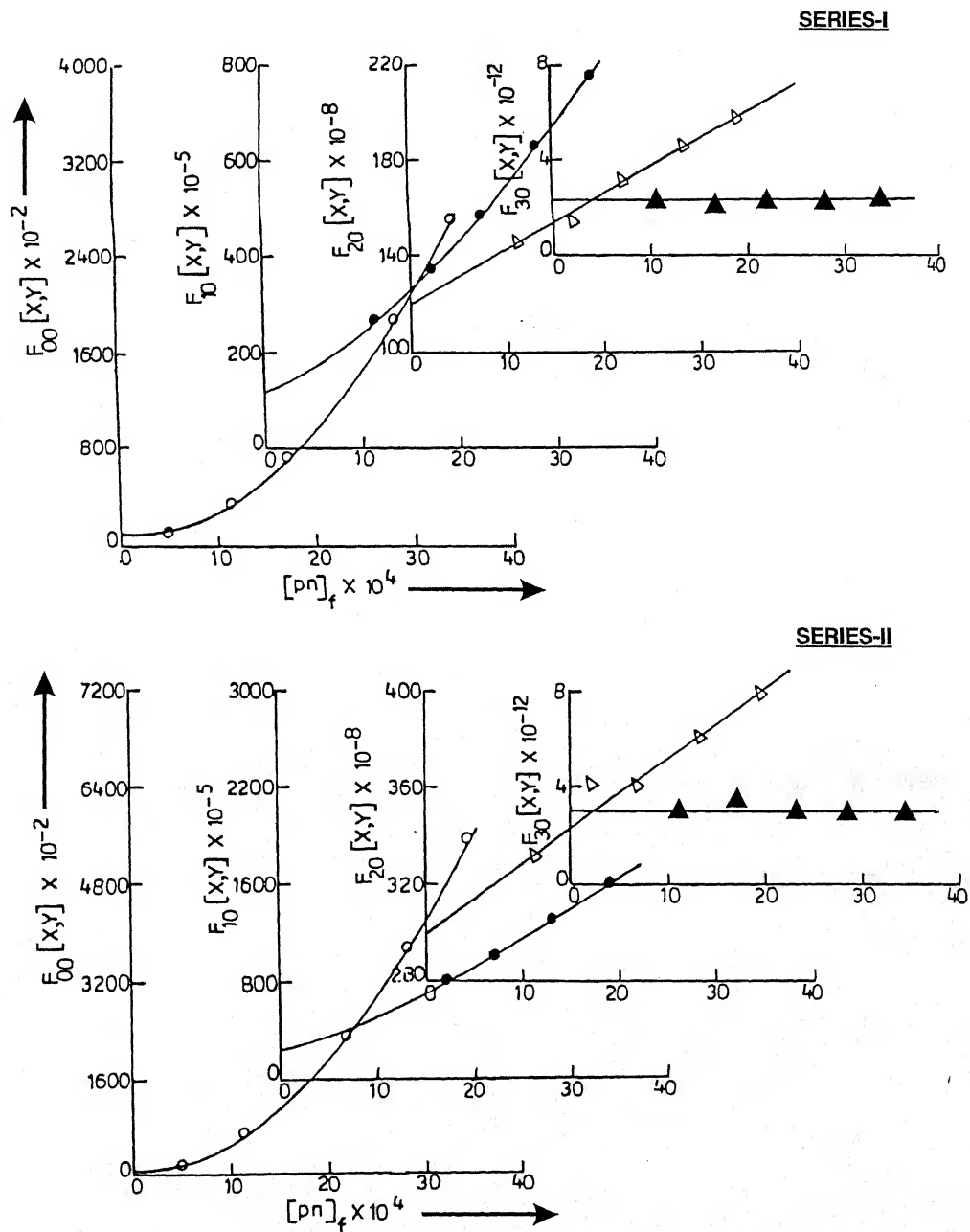


FIG. 3.37 PLOT OF $F_i [X,Y]$ FUNCTIONS FOR Cd(II) - PROPYLENEDIAMINE - DL - ALANINE SYSTEM

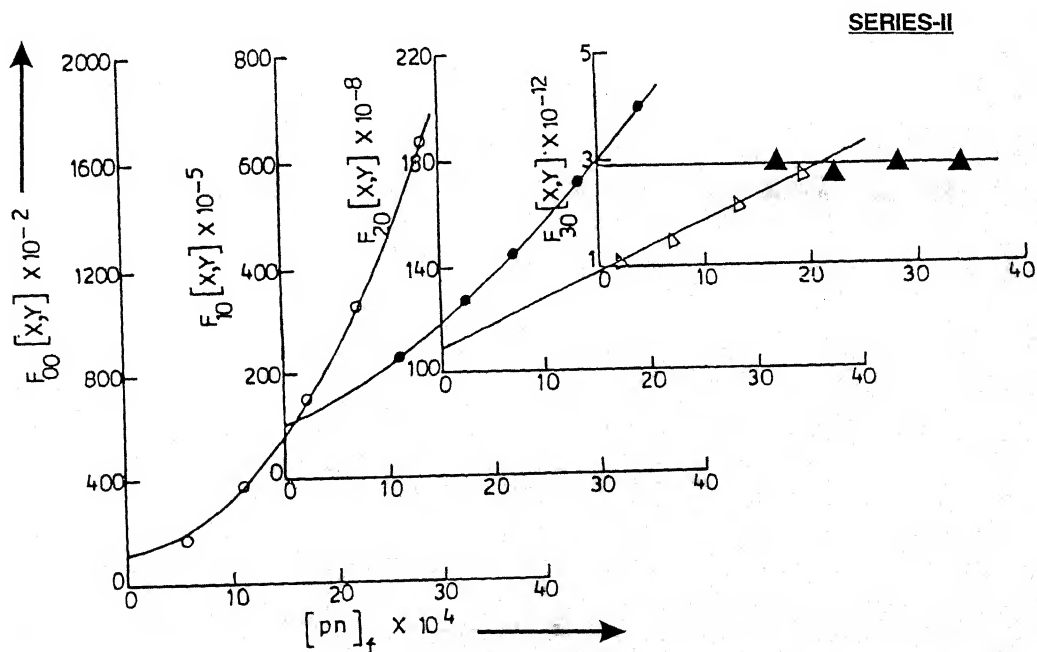
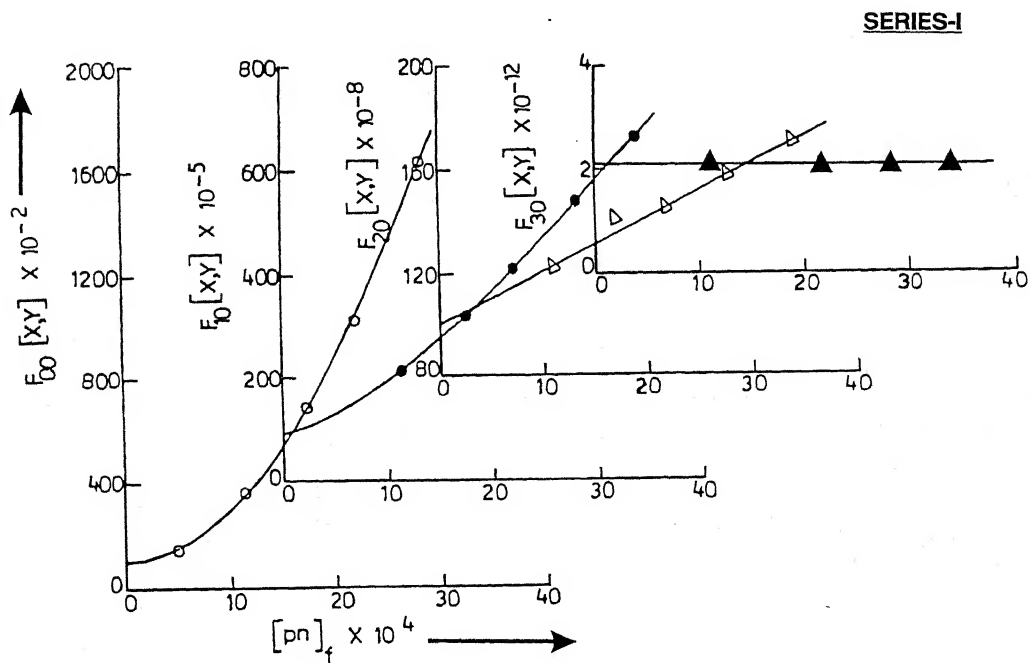


FIG. 3.38 POLT OF $F_0[X,Y]$ FUNCTIONS FOR Cd (II) - PROPYLENEDIAMINE - DL - VALINE SYSTEM

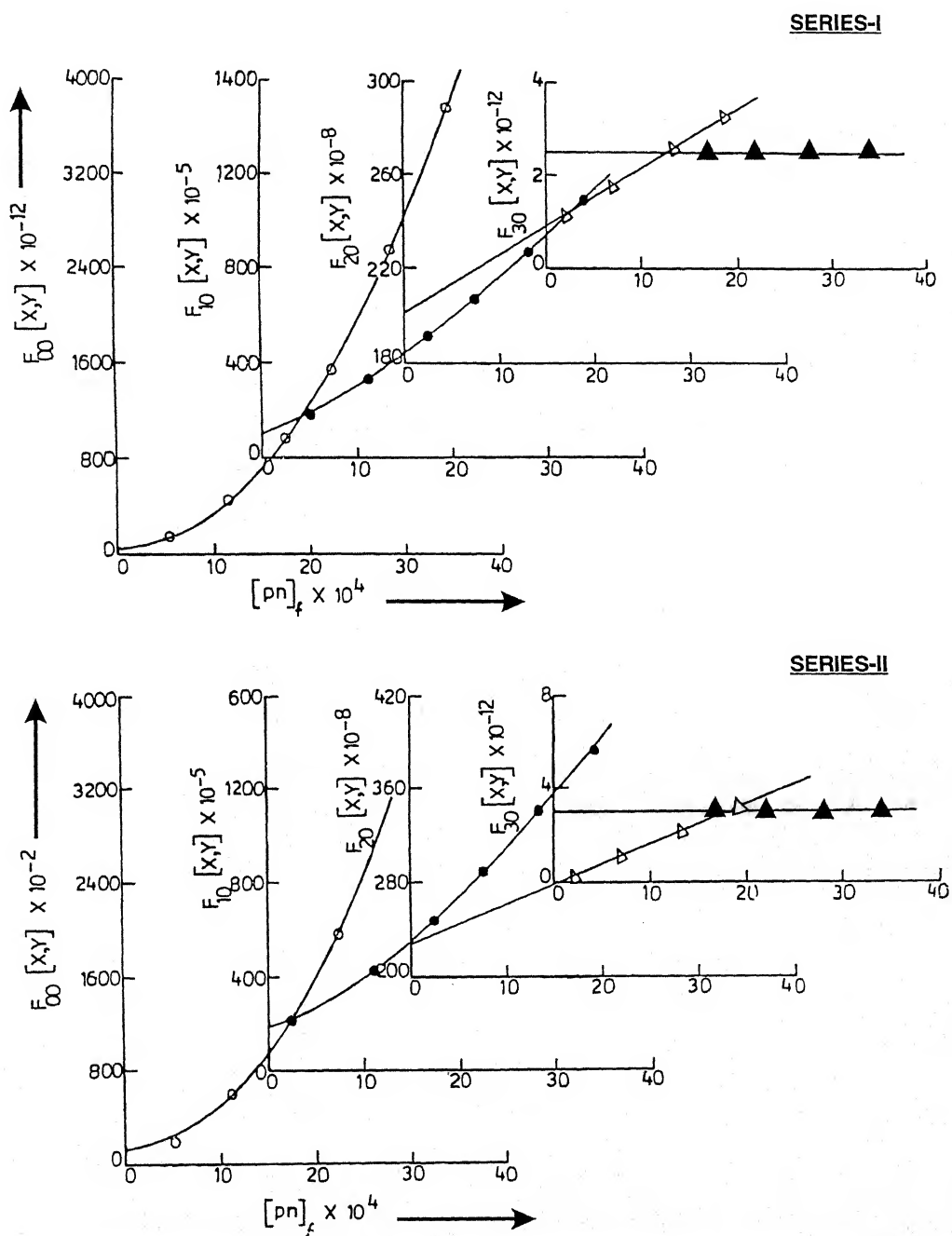


FIG. 3.39 POLT OF $F_i[X,Y]$ FUNCTIONS FOR Cd(II) - PROPYLENEDIAMINE - L - ISOLEUCINE SYSTEM

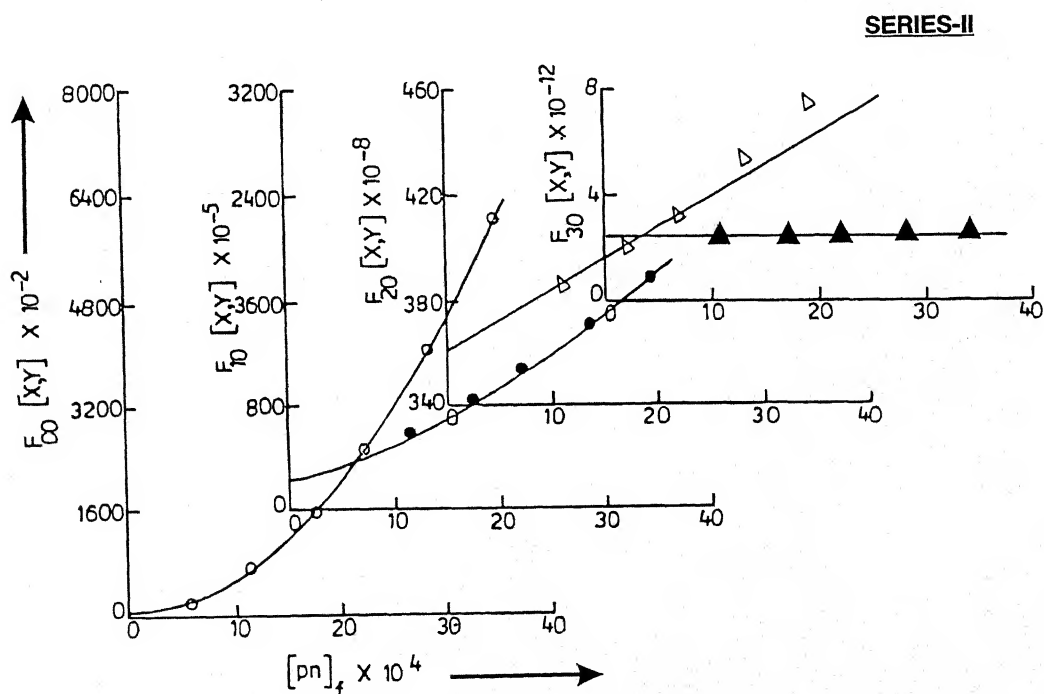
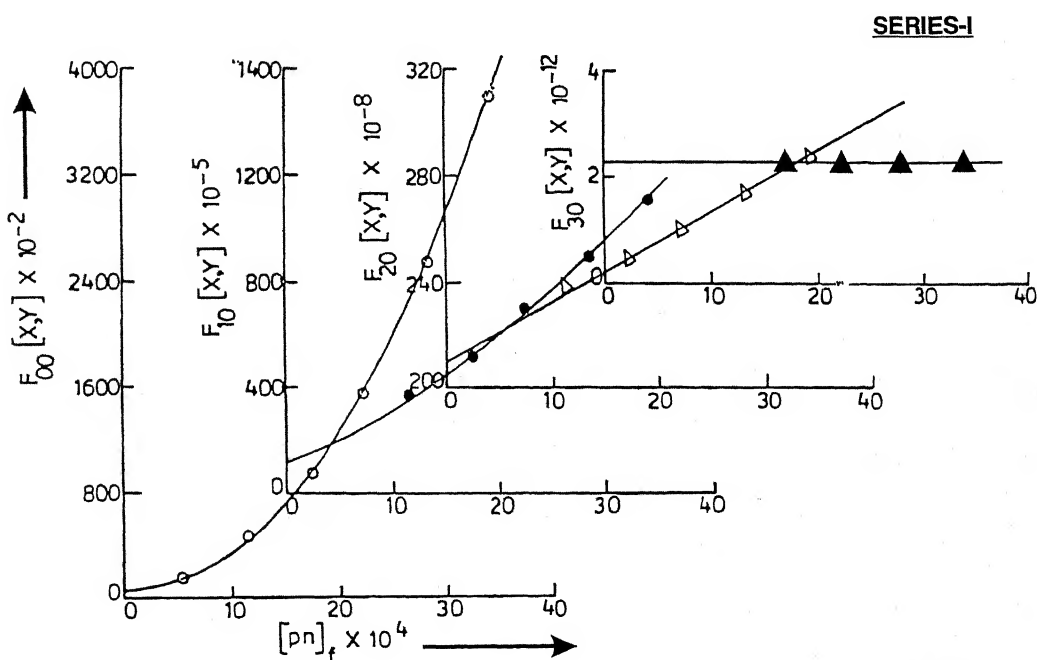


FIG. 3.40 POLT OF $F_i [X,Y]$ FUNCTIONS FOR Cd (II) - PROPYLENEDIAMINE - L - TRYPTOPHANE SYSTEM

TABLE 3.01

POLAROGRAPHIC FUNCTIONS OF THE SIMPLE Cd (II) - ETHYLENEDIAMINE SYSTEM

$[\text{en}]_t$ X 10^3 M	$[\text{en}]_f$ X 10^4 M	$\log \frac{I_M}{I_c}$	$\Delta E_{1/2}$ V	Slope mV	$F_0 [x]$ X 10^{-2}	$F_1 [x]$ X 10^{-6}	$F_2 [x]$ X 10^{-8}	$F_3 [x]$ X 10^{-12}
0.0	0.0	—	—	29	—	—	—	—
2.0	3.0	.0082	0.089	30	10.48	3.49	69.81	—
4.0	6.0	.0180	0.106	31	40.34	6.72	88.70	—
6.0	9.0	.0426	0.117	31	98.35	10.92	105.85	2.65
8.0	12.0	.0435	0.124	31	174.02	14.50	109.17	2.26
10.0	15.0	.0521	0.130	30	283.27	18.88	116.56	2.30
12.0	18.0	.0558	0.135	31	421.93	23.44	122.44	2.24

$[\text{en}]_t$ = Total (analytical) concentration of ethylenediamine (en)

$[\text{en}]_f$ = Free ligand concentration of ethylenediamine (en)

$[\text{Cd}^{2+}] = 1.0 \times 10^{-3} \text{ M}$, $\mu = 1.0$ (NaNO_3), pH = 8.2, Temp. = $25 \pm 0.1^\circ\text{C}$

TABLE 3.02

POLAROGRAPHIC FUNCTIONS OF THE SIMPLE Cd (II) - PROPYLENEDIAMINE SYSTEM

$[\text{pn}]_t$ X 10^3 M	$[\text{pn}]_f$ X 10^4 M	$\log \frac{I_M}{I_c}$	$\Delta E_{1/2}$ V	Slope mV	F_0 [x] X 10^{-4}	F_1 [x] X 10^{-5}	F_2 [x] X 10^{-8}	F_3 [x] X 10^{-12}
0.0	0.0	—	—	29	—	—	—	—
2.0	5.0	.0033	0.100	29	24.46	48.91	—	—
4.0	11.0	.0096	0.121	30	127.54	115.94	79.94	—
6.0	17.00	.0165	0.133	30	330.10	194.17	97.74	1.92
8.0	22.0	.0230	0.140	30	578.20	262	106.73	1.90
10.0	28.00	.306	0.147	31	1015.35	362.62	119.50	1.94
12.0	34.0	.0352	0.152	31	1515.50	445.73	130.86	1.93

$[\text{pn}]_t$ = Total (analytical) concentration of propylenediamine (pn)

$[\text{pn}]_f$ = Free ligand concentration of propylenediamine (pn)

$[\text{Cd}^{2+}] = 1.0 \times 10^{-3} \text{ M}$, $\mu = 1.0$ (NaNO_3), pH = 8.2, Temp. = $25 \pm 0.1^\circ\text{C}$

TABLE 3.03

POLAROGRAPHIC FUNCTIONS OF THE SIMPLE Cd (II) - GLYCINE SYSTEM

[gly] M	[gly ⁻] X 10 ⁴ M	log $\frac{I_M}{I_c}$	$\Delta E_{1/2}$	Slope mV	F ₀ [x]	F ₁ [x] X 10 ⁻⁴	F ₂ [x] X 10 ⁻⁷	F ₃ [x] X 10 ⁻¹⁰
0.00	0.0	—	—	29	—	—	—	—
0.01	2.5	.0072	0.126	29	7.71	2.68	—	—
0.02	5.0	.0170	0.140	30	23.48	4.49	4.59	3.18
0.04	10.0	.0347	0.156	30	85.14	8.41	6.21	3.21
0.06	15.0	.0347	0.168	30	216.89	14.39	8.12	3.41
0.08	20.0	0.0420	0.177	31	444.88	22.19	9.99	3.48
0.10	25.0	.0451	0.184	31	773.27	30.89	11.48	3.40

[gly] = Total (analytical) concentration of glycine (gly)

[gly⁻] = Glycinate ion concentration.

[Cd²⁺] = 1.0 X 10⁻³ M, μ = 1.0 (NaNO₃), pH = 8.2, Temp. = 25 ± 0.1°C

TABLE 3.04

POLAROGRAPHIC FUNCTIONS OF THE SIMPLE Cd (II) - DL - ALANINE SYSTEM

[ala] M	[ala ⁻] X 10 ⁴ M	log $\frac{I_M}{I_c}$	$\Delta E_{1/2}$ V	Slope mV	F ₀ [x]	F ₁ [x] X 10 ⁻³	F ₂ [x] X 10 ⁻⁵	F ₃ [x] X 10 ⁻⁹
0.00	0.0	—	—	29	—	—	—	—
0.02	4.0	.0034	0.132	29	12.20	28.00	200.11	—
0.04	8.00	.0072	0.145	30	33.91	41.13	264.24	3.03
0.06	12.00	.0170	0.153	30	64.68	53.07	275.61	3.00
0.08	16.00	.0301	0.159	30	106.43	65.89	286.85	2.92
0.10	20.00	.0301	0.164	31	157.15	78.08	300.38	3.01
0.12	25.0	.0301	0.170	31	250.75	99.90	309.60	3.18

[ala] = Total (analytical) concentration of alanine (ala)

[ala⁻] = Alaninate ion concentration.

[Cd²⁺] = 1.0 X 10⁻³ M, μ = 1.0 (NaNO₃), pH = 8.2, Temp. = 25 ± 0.1°C

TABLE 3.05

POLAROGRAPHIC FUNCTIONS OF THE SIMPLE Cd (II) - DL - VALINE SYSTEM

[val] M	[val ⁻] X 10 ⁴ M	log $\frac{I_M}{I_c}$	$\Delta E_{1/2}$ V	Slope mV	F ₀ [x]	F ₁ [x] X 10 ⁻³	F ₂ [x] X 10 ⁻⁵	F ₃ [x] X 10 ⁻⁹
0.00	0.00	—	—	29	—	—	—	—
0.02	5.00	.0347	0.130	30	11.22	20.44	—	—
0.04	11.00	.0735	0.145	30	39.50	35.00	200.03	—
0.06	17.00	.1015	0.154	30	84.95	49.38	214.02	4.94
0.08	23.00	.1075	0.162	31	160.72	69.44	245.41	5.01
0.10	29.00	.1313	0.168	31	271.00	93.11	276.23	5.04
0.12	35.00	.1538	0.173	31	421.41	120.12	306.04	5.02

[val] = Total (analytical) concentration of valine (val)

[val⁻] = Valinate ion concentration.

[Cd²⁺] = 1.0 X 10⁻³ M, μ = 1.0 (NaNO₃), pH = 8.2, Temp. = 25 ± 0.1°C

TABLE 3.06

POLAROGRAPHIC FUNCTIONS OF THE SIMPLE Cd (II) - L - ISOLEUCINE SYSTEM

[isolc] M	[isolc ⁻] X 10 ⁴ M	log $\frac{I_M}{I_c}$	$\Delta E_{1/2}$ V	Slope mV	F ₀ [x]	F ₁ [x] X 10 ⁻³	F ₂ [x] X 10 ⁻⁶	F ₃ [x] X 10 ⁻⁹
0.00	0.0	—	—	29	—	—	—	—
0.01	2.0	.0048	0.120	29	4.80	19.02	15.11	—
0.02	5.0	.0096	0.133	30	13.38	24.77	17.54	8.07
0.03	8.0	.0096	0.142	30	26.99	32.49	20.61	8.89
0.04	10.0	.0285	0.146	30	38.50	37.51	21.51	8.01
0.05	13.0	.0342	0.152	31	62.25	47.12	23.93	8.02
0.06	16.0	.0441	0.157	31	94.06	58.16	26.35	8.03

[isolc] = Total (analytical) concentration of isoleucine (isolc)

[isolc⁻] = Isoleucinate ion concentration.

[Cd²⁺] = 1.0 X 10⁻³ M, μ = 1.0 (NaNO₃), pH = 8.2, Temp. = 25 ± 0.1°C

TABLE 3.07

POLAROGRAPHIC FUNCTIONS OF THE SIMPLE Cd (II) - L - TRYPTOPHAN SYSTEM

[try] M	[try ⁻] X 10 ⁴ M	log $\frac{I_M}{I_c}$	$\Delta E_{1/2}$	Slope
0.00	0.0	—	—	30
0.01	6.0	0.1634	0.139	30
0.02	12.0	0.1704	0.156	31
0.03	18.0	0.1761	0.168	31
0.04	24.0	0.1848	0.178	31
0.05	30.0	0.1899	0.184	30
0.06	36.0	0.1951	0.192	31

[try] = Total (analytical) concentration of tryptophan (try)

[try⁻] = Tryptophan ion concentration.

[Cd²⁺] = 1.0 X 10⁻³ M, μ = 1.0 (NaNO₃), pH = 8.2, Temp. = 25 ± 0.1°C

TABLE 3.08

POLAROGRAPHIC FUNCTIONS OF MIXED Cd (II) - ETHYLENEDIAMINEGLYCINE SYSTEM

$[en]_t$	$[en]_f$	$\log \frac{I_M}{I_c}$	$\Delta E_{1/2}$	Slope	$F_{00} [X,Y]$	$F_{10} [X,Y]$	$F_{20} [X,Y]$	$F_{30} [X,Y]$
$\times 10^3$	$\times 10^4$		V	mV	$\times 10^{-3}$	$\times 10^{-6}$	$\times 10^{-8}$	$\times 10^{-12}$
M	M							
2.0	3.0	—	—	29	2.89	—	—	—
4.0	6.0	.0025	0.023	30	17.52	17.53	92.15	—
6.0	9.0	.0144	0.031	31	33.58	29.53	194.88	2.76
8.0	12.0	.0159	0.036	31	49.77	35.64	197.03	2.25
10.0	15.0	.0159	0.041	30	73.49	44.32	215.51	3.03
12.0	18.0	.0164	0.045	31	100.48	51.93	221.88	2.88

SERIES I : $[gly] = 0.01 \text{ M}$

$[en]_t$	$[en]_f$	$\log \frac{I_M}{I_c}$	$\Delta E_{1/2}$	Slope	$F_{00} [X,Y]$	$F_{10} [X,Y]$	$F_{20} [X,Y]$	$F_{30} [X,Y]$
$\times 10^3$	$\times 10^4$		V	mV	$\times 10^{-3}$	$\times 10^{-6}$	$\times 10^{-8}$	$\times 10^{-12}$
M	M							
2.0	3.0	—	—	29	4.65	—	—	—
4.0	6.0	.0084	0.020	29	22.54	24.23	53.83	—
6.0	9.0	.0109	0.028	30	42.28	38.09	189.94	—
8.0	12.0	.0236	0.033	30	64.30	46.92	216.01	3.00
10.0	15.0	.0341	0.037	30	89.97	54.65	224.32	2.95
12.0	18.0	.0362	0.749	31	121.84	63.24	234.71	3.03

SERIES II : $[gly] = 0.02 \text{ M}$ $[Cd^{2+}] = 1.0 \times 10^{-3} \text{ M}$, $\mu = 1.0 \text{ (NaNO}_3\text{)}$, $pH = 8.2$, $Temp. = 25 \pm 0.1^\circ C$

TABLE 3.09

POLAROGRAPHIC FUNCTIONS OF MIXED Cd (II) - ETHYLENEDIAMINE**- DL - ALANINE SYSTEM**

$[en]_t$	$[en]_f$	$\log \frac{I_M}{I_c}$	$\Delta E_{1/2}$	Slope	$F_{00} [X,Y]$	$F_{10} [X,Y]$	$F_{20} [X,Y]$	$F_{30} [X,Y]$
$\times 10^3$	$\times 10^4$		V	mV	$\times 10^{-3}$	$\times 10^{-6}$	$\times 10^{-8}$	$\times 10^{-12}$
M	M							
2.0	3.0	—	—	29	3.64	—	—	—
4.0	6.0	.0039	0.020	29	17.48	19.13	135.47	—
6.0	9.0	.0078	0.028	30	32.90	29.89	209.92	1.99
8.0	12.0	.0083	0.034	30	52.55	37.13	217.76	2.14
10.0	15.0	.0148	0.038	30	72.88	44.59	223.93	2.12
12.0	18.0	.0198	0.042	31	100.72	52.62	231.25	2.17

SERIES I : $[ala] = 0.02 \text{ M}$

$[en]_t$	$[en]_f$	$\log \frac{I_M}{I_c}$	$\Delta E_{1/2}$	Slope	$F_{00} [X,Y]$	$F_{10} [X,Y]$	$F_{20} [X,Y]$	$F_{30} [X,Y]$
$\times 10^3$	$\times 10^4$		V	mV	$\times 10^{-3}$	$\times 10^{-6}$	$\times 10^{-8}$	$\times 10^{-12}$
M	M							
2.0	3.0	—	—	29	4.60	—	—	—
4.0	6.0	.0010	0.020	29	21.93	23.22	120.38	—
6.0	9.0	.0024	0.028	30	41.03	36.69	229.99	2.33
8.0	12.0	.0068	0.033	30	61.24	44.37	236.41	2.28
10.0	15.0	.0229	0.037	31	86.79	52.53	243.54	2.30
12.0	18.0	.0229	0.041	31	118.55	61.41	252.31	2.40

SERIES II : $[ala] = 0.04 \text{ M}$ $[Cd^{2+}] = 1.0 \times 10^{-3} \text{ M}$, $\mu = 1.0$ ($NaNO_3$), $pH = 8.2$, $Temp. = 25 \pm 0.1^\circ C$

TABLE 3.10

POLAROGRAPHIC FUNCTIONS OF MIXED Cd (II) - ETHYLENEDIAMINE**- DL - VALINE SYSTEM**

$[en]_t$	$[en]_f$	$\log \frac{I_M}{I_c}$	$\Delta E_{1/2}$	Slope	$F_{00} [X,Y]$	$F_{10} [X,Y]$	$F_{20} [X,Y]$	$F_{30} [X,Y]$
$\times 10^3$	$\times 10^4$		V	mV	$\times 10^{-3}$	$\times 10^{-6}$	$\times 10^{-8}$	$\times 10^{-12}$
M	M							
2.0	3.0	—	—	29	3.39	—	—	—
4.0	6.0	.0020	0.021	30	17.49	17.49	91.59	—
6.0	9.0	.0159	0.029	30	33.71	29.67	196.41	1.82
8.0	12.0	.0225	0.034	31	50.53	32.28	202.32	1.86
10.0	15.0	.0387	0.038	31	71.65	43.10	207.33	1.82
12.0	18.0	.0387	0.042	31	97.76	50.42	213.46	1.85

SERIES I : [val] = 0.02 M

$[en]_t$	$[en]_f$	$\log \frac{I_M}{I_c}$	$\Delta E_{1/2}$	Slope	$F_{00} [X,Y]$	$F_{10} [X,Y]$	$F_{20} [X,Y]$	$F_{30} [X,Y]$
$\times 10^3$	$\times 10^4$		V	mV	$\times 10^{-3}$	$\times 10^{-6}$	$\times 10^{-8}$	$\times 10^{-12}$
M	M							
2.0	3.0	—	—	29	5.27	—	—	—
4.0	6.0	.0049	0.014	29	15.83	13.05	—	—
6.0	9.0	.0062	0.028	29	47.35	43.72	207.99	1.99
8.0	12.0	.0329	0.032	30	68.81	50.68	213.99	1.99
10.0	15.0	.0371	0.036	30	94.79	57.86	219.08	1.93
12.0	18.0	.0594	0.039	31	126.19	65.66	225.89	1.99

SERIES II : [val] = 0.04 M $[Cd^{2+}] = 1.0 \times 10^{-3} \text{ M}$, $\mu = 1.0$ (NaNO₃), pH = 8.2, Temp. = $25 \pm 0.1^\circ\text{C}$

TABLE 3.11

POLAROGRAPHIC FUNCTIONS OF MIXED Cd (II) - ETHYLENEDIAMINE
- L - ISOLEUCINE SYSTEM

$[en]_t$	$[en]_f$	$\log \frac{I_M}{I_c}$	$\Delta E_{1/2}$	Slope	$F_{00} [X,Y]$	$F_{10} [X,Y]$	$F_{20} [X,Y]$	$F_{30} [X,Y]$
$\times 10^3$	$\times 10^4$		V	mV	$\times 10^{-3}$	$\times 10^{-6}$	$\times 10^{-8}$	$\times 10^{-12}$
M	M							
2.0	3.0	—	—	29	7.27	—	—	—
4.0	6.0	.0033	0.013	30	20.20	22.00	166.68	—
6.0	9.0	.0067	0.020	30	35.11	31.23	213.67	1.74
8.0	12.0	.0126	0.025	31	52.88	38.23	218.65	1.72
10.0	15.0	.0334	0.033	31	75.33	45.55	223.69	1.71
12.0	18.0	.0334	0.033	31	102.88	53.27	229.28	1.73

SERIES I : [Isolc] = 0.01 M

$[en]_t$	$[en]_f$	$\log \frac{I_M}{I_c}$	$\Delta E_{1/2}$	Slope	$F_{00} [X,Y]$	$F_{10} [X,Y]$	$F_{20} [X,Y]$	$F_{30} [X,Y]$
$\times 10^3$	$\times 10^4$		V	mV	$\times 10^{-3}$	$\times 10^{-6}$	$\times 10^{-8}$	$\times 10^{-12}$
M	M							
2.0	3.0	—	—	29	8.54	—	—	—
4.0	6.0	.0024	0.015	29	27.65	29.41	173.54	—
6.0	9.0	.0063	0.021	29	44.53	38.36	215.17	—
8.0	12.0	.0063	0.026	30	65.75	46.45	228.80	1.90
10.0	15.0	.0127	0.030	31	91.13	54.09	233.92	1.86
12.0	18.0	.0132	0.034	31	124.55	62.53	241.84	1.98

SERIES II : [Isolc] = 0.02 M

[Cd²⁺] = 1.0 $\times 10^{-3}$ M, μ = 1.0 (NaNO₃), pH = 8.2, Temp. = 25 \pm 0.1°C

TABLE 3.12

POLAROGRAPHIC FUNCTIONS OF MIXED Cd (II) - ETHYLENEDIAMINE**- L - TRYPTOPHAN SYSTEM**

$[en]_t$	$[en]_f$	$\log \frac{I_M}{I_c}$	$\Delta E_{1/2}$	Slope	$F_{00} [X,Y]$	$F_{10} [X,Y]$	$F_{20} [X,Y]$	$F_{30} [X,Y]$
$\times 10^3$	$\times 10^4$		V	mV	$\times 10^{-2}$	$\times 10^{-5}$	$\times 10^{-8}$	$\times 10^{-12}$
M	M							
2.0	3.0	—	—	29	33.75	—	—	—
4.0	6.0	.0078	0.022	29	191.12	201.87	128.12	—
6.0	9.0	.0098	0.029	29	331.31	290.34	183.72	2.07
8.0	12.0	.0138	0.034	30	493.61	353.01	190.01	2.08
10.0	15.0	.0291	0.038	31	698.50	419.00	196.00	2.06
12.0	18.0	.0291	0.042	31	954.03	491.26	203.40	2.13

SERIES I : [try] = 0.01 M

$[en]_t$	$[en]_f$	$\log \frac{I_M}{I_c}$	$\Delta E_{1/2}$	Slope	$F_{00} [X,Y]$	$F_{10} [X,Y]$	$F_{20} [X,Y]$	$F_{30} [X,Y]$
$\times 10^3$	$\times 10^4$		V	mV	$\times 10^{-2}$	$\times 10^{-5}$	$\times 10^{-8}$	$\times 10^{-12}$
M	M							
2.0	3.0	—	—	29	46.27	—	—	—
4.0	6.0	.0124	0.022	30	264.61	291.02	151.69	—
6.0	9.0	.0159	0.028	31	425.88	373.21	192.45	—
8.0	12.0	.0164	0.033	30	629.40	449.51	207.92	2.15
10.0	15.0	.0225	0.037	30	871.61	521.07	214.05	2.13
12.0	18.0	.0230	0.041	31	1192.49	595.82	219.90	2.10

SERIES II : [try] = 0.02 M

[Cd²⁺] = 1.0 $\times 10^{-3}$ M, μ = 1.0 (NaNO₃), pH = 8.2, Temp. = 25 \pm 0.1°C

TABLE 3.13

POLAROGRAPHIC FUNCTIONS OF MIXED Cd (II) - PROPYLENEDIAMINEGLYCINE SYSTEM

$[pn]_t$	$[pn]_f$	$\log \frac{I_M}{I_c}$	$\Delta E_{1/2}$	Slope	$F_{00} [X,Y]$	$F_{10} [X,Y]$	$F_{20} [X,Y]$	$F_{30} [X,Y]$
$\times 10^3$	$\times 10^4$		V	mV	$\times 10^{-2}$	$\times 10^{-6}$	$\times 10^{-8}$	$\times 10^{-12}$
M	M							
2.0	5.0	—	—	29	131.51	10.30	—	—
4.0	11.0	.0112	0.019	30	593.04	46.64	205.82	—
6.0	17.0	.0112	0.027	29	1107.00	60.41	214.19	—
8.0	22.0	.0112	0.033	30	1767.00	76.68	239.46	2.24
10.0	28.0	.0296	0.038	30	2721.40	94.33	251.12	2.20
12.0	34.0	.0296	0.043	31	4018.20	115.83	270.08	2.35

SERIES I : $[gly] = 0.01 \text{ M}$

$[pn]_t$	$[pn]_f$	$\log \frac{I_M}{I_c}$	$\Delta E_{1/2}$	Slope	$F_{00} [X,Y]$	$F_{10} [X,Y]$	$F_{20} [X,Y]$	$F_{30} [X,Y]$
$\times 10^3$	$\times 10^4$		V	mV	$\times 10^{-2}$	$\times 10^{-5}$	$\times 10^{-8}$	$\times 10^{-12}$
M	M							
2.0	5.0	—	—	29	175.98	—	—	—
4.0	11.0	.0125	0.019	29	796.29	63.29	302.72	—
6.0	17.0	.0228	0.028	29	1643.26	90.78	357.53	—
8.0	22.0	.0228	0.034	30	2622.96	114.68	384.91	2.50
10.0	28.0	.0228	0.040	31	4189.37	145.33	401.19	2.54
12.0	34.0	.0381	0.044	31	5926.12	171.35	415.75	2.52

SERIES II : $[gly] = 0.02 \text{ M}$ $[Cd^{2+}] = 1.0 \times 10^{-3} \text{ M}$, $\mu = 1.0$ ($NaNO_3$), $pH = 8.2$, $Temp. = 25 \pm 0.1^\circ C$

TABLE 3.14

POLAROGRAPHIC FUNCTIONS OF MIXED Cd (II) - PROPYLENEDIAMINE- DL - ALANINE SYSTEM

$[pn]_t$	$[pn]_f$	$\log \frac{I_M}{I_c}$	$\Delta E_{1/2}$	Slope	$F_{00} [X,Y]$	$F_{10} [X,Y]$	$F_{20} [X,Y]$	$F_{30} [X,Y]$
$\times 10^3$	$\times 10^4$		V	mV	$\times 10^{-2}$	$\times 10^{-5}$	$\times 10^{-8}$	$\times 10^{-12}$
M	M							
2.0	5.0	—	—	29	85.73	11.46	—	—
4.0	11.0	.0010	0.019	29	378.04	270.95	146.32	2.40
6.0	17.0	.0143	0.027	30	727.28	380.75	159.27	2.31
8.0	22.0	.0143	0.033	30	1160.68	491.22	173.28	2.42
10.0	28.0	.0143	0.039	30	1856.95	634.62	187.36	2.40
12.0	34.0	.0224	0.044	31	2787.38	796.29	201.85	2.41

SERIES I : $[ala] = 0.02 \text{ M}$

$[pn]_t$	$[pn]_f$	$\log \frac{I_M}{I_c}$	$\Delta E_{1/2}$	Slope	$F_{00} [X,Y]$	$F_{10} [X,Y]$	$F_{20} [X,Y]$	$F_{30} [X,Y]$
$\times 10^3$	$\times 10^4$		V	mV	$\times 10^{-2}$	$\times 10^{-5}$	$\times 10^{-8}$	$\times 10^{-12}$
M	M							
2.0	5.0	—	—	29	159.89	119.78	—	—
4.0	11.0	.0039	0.020	30	766.78	606.26	332.88	3.00
6.0	17.0	.0039	0.029	31	1546.36	839.04	352.37	3.08
8.0	22.0	.0068	0.035	31	2485.05	1070.48	377.49	3.06
10.0	28.0	.0203	0.040	31	3784.82	1316.01	384.29	3.01
12.0	34.0	.0203	0.045	31	5583.03	1612.65	403.72	3.05

SERIES II : $[ala] = 0.04 \text{ M}$ $[Cd^{2+}] = 1.0 \times 10^{-3} \text{ M}$, $\mu = 1.0 \text{ (NaNO}_3\text{)}$, $pH = 8.2$, $Temp. = 25 \pm 0.1^\circ C$

TABLE 3.15

POLAROGRAPHIC FUNCTIONS OF MIXED Cd (II) - PROPYLENEDIAMINE**- DL - VALINE SYSTEM**

$[pn]_t$	$[pn]_f$	$\log \frac{I_M}{I_c}$	$\Delta E_{1/2}$	Slope	$F_{00} [X,Y]$	$F_{10} [X,Y]$	$F_{20} [X,Y]$	$F_{30} [X,Y]$
$\times 10^3$	$\times 10^4$		V	mV	$\times 10^{-2}$	$\times 10^{-5}$	$\times 10^{-8}$	$\times 10^{-12}$
M	M							
2.0	5.0	—	—	29	151.94	63.88	—	—
4.0	11.0	.0116	0.011	29	367.61	225.11	122.83	2.07
6.0	17.0	.0116	0.019	30	686.19	321.29	136.05	2.12
8.0	22.0	.0167	0.024	31	1024.75	411.25	146.02	2.10
10.0	28.0	.0172	0.030	30	1636.46	341.59	161.28	2.18
12.0	34.0	.0172	0.035	31	2419.05	676.19	172.41	2.12

SERIES I : [val] = 0.02 M

$[pn]_t$	$[pn]_f$	$\log \frac{I_M}{I_c}$	$\Delta E_{1/2}$	Slope	$F_{00} [X,Y]$	$F_{10} [X,Y]$	$F_{20} [X,Y]$	$F_{30} [X,Y]$
$\times 10^3$	$\times 10^4$		V	mV	$\times 10^{-2}$	$\times 10^{-5}$	$\times 10^{-8}$	$\times 10^{-12}$
M	M							
2.0	5.0	—	—	29	158.82	77.65	—	—
4.0	11.0	.0015	0.011	30	375.96	232.69	120.63	—
6.0	17.0	.0034	0.019	29	703.11	343.01	142.95	1.93
8.0	22.0	.0107	0.024	30	1056.80	434.91	152.23	1.92
10.0	28.0	.0107	0.030	30	1686.76	559.56	164.13	1.93
12.0	34.0	.0122	0.035	31	2499.15	699.75	176.39	1.95

SERIES II : [val] = 0.04 M[Cd²⁺] = 1.0 $\times 10^{-3}$ M, μ = 1.0 (NaNO₃), pH = 8.2, Temp. = 25 \pm 0.1°C

TABLE 3.16

POLAROGRAPHIC FUNCTIONS OF MIXED Cd (II) - PROPYLENEDIAMINE- L - ISOLEUCINE SYSTEM

$[pn]_t$	$[pn]_f$	$\log \frac{I_M}{I_c}$	$\Delta E_{1/2}$	Slope	$F_{00} [X,Y]$	$F_{10} [X,Y]$	$F_{20} [X,Y]$	$F_{30} [X,Y]$
$\times 10^3$	$\times 10^4$		V	mV	$\times 10^{-2}$	$\times 10^{-5}$	$\times 10^{-8}$	$\times 10^{-12}$
M	M							
2.0	5.0	—	—	29	162.04	164.08	—	—
4.0	11.0	.0039	0.013	30	450.44	336.77	197.06	—
6.0	17.0	.0059	0.023	31	985.42	532.63	242.72	2.51
8.0	22.0	.0074	0.029	29	1577.99	680.91	254.96	2.50
10.0	28.0	.0104	0.035	30	2536.70	877.39	270.49	2.51
12.0	34.0	.0139	0.040	31	3775.99	1087.06	284.43	2.48

SERIES I : $[Isolc] = 0.01 \text{ M}$

$[pn]_t$	$[pn]_f$	$\log \frac{I_M}{I_c}$	$\Delta E_{1/2}$	Slope	$F_{00} [X,Y]$	$F_{10} [X,Y]$	$F_{20} [X,Y]$	$F_{30} [X,Y]$
$\times 10^3$	$\times 10^4$		V	mV	$\times 10^{-2}$	$\times 10^{-5}$	$\times 10^{-8}$	$\times 10^{-12}$
M	M							
2.0	5.0	—	—	29	171.69	—	—	—
4.0	11.0	.0088	0.016	29	609.58	445.07	240.97	—
6.0	17.0	.0097	0.025	30	1232.15	654.20	278.94	2.90
8.0	22.0	.0117	0.031	31	1975.83	843.56	301.62	3.25
10.0	28.0	.0117	0.037	30	3153.90	1079.96	321.42	3.26
12.0	34.0	.0127	0.042	31	4667.40	1337.47	340.43	3.24

SERIES II : $[Isolc] = 0.02 \text{ M}$ $[Cd^{2+}] = 1.0 \times 10^{-3} \text{ M}$, $\mu = 1.0$ ($NaNO_3$), $pH = 8.2$, $Temp. = 25 \pm 0.1^\circ C$

TABLE 3.17

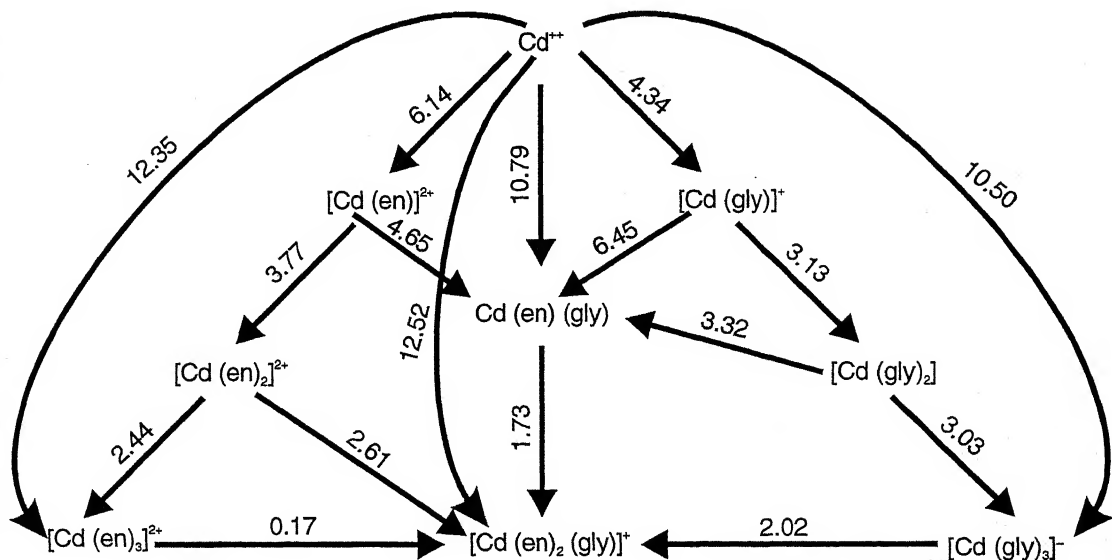
POLAROGRAPHIC FUNCTIONS OF MIXED Cd (II) - PROPYLENEDIAMINE**- L - TRYPTOPHAN SYSTEM**

$[pn]_t$	$[pn]_f$	$\log \frac{I_M}{I_c}$	$\Delta E_{1/2}$	Slope	$F_{00} [X,Y]$	$F_{10} [X,Y]$	$F_{20} [X,Y]$	$F_{30} [X,Y]$
$\times 10^3$	$\times 10^4$		V	mV	$\times 10^{-2}$	$\times 10^{-5}$	$\times 10^{-8}$	$\times 10^{-12}$
M	M							
2.0	5.0	—	—	30	117.79	115.59	—	—
4.0	11.0	.0025	0.018	31	481.94	383.58	239.62	2.69
6.0	17.0	.0089	0.027	30	986.51	545.00	250.00	2.35
8.0	22.0	.0119	0.033	29	1585.28	693.31	260.59	2.30
10.0	28.0	.0159	0.039	30	2553.83	890.65	275.23	2.32
12.0	34.0	.0189	0.044	31	3797.79	1099.35	288.04	2.30

SERIES I : $[try] = 0.01 \text{ M}$

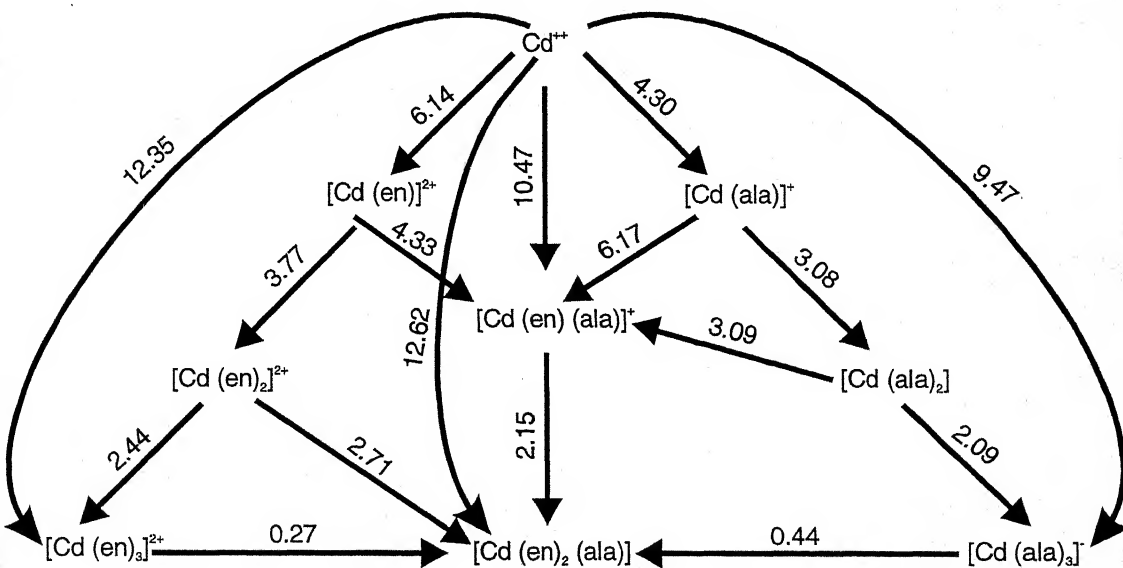
$[pn]_t$	$[pn]_f$	$\log \frac{I_M}{I_c}$	$\Delta E_{1/2}$	Slope	$F_{00} [X,Y]$	$F_{10} [X,Y]$	$F_{20} [X,Y]$	$F_{30} [X,Y]$
$\times 10^3$	$\times 10^4$		V	mV	$\times 10^{-2}$	$\times 10^{-5}$	$\times 10^{-8}$	$\times 10^{-12}$
M	M							
2.0	5.0	—	—	29	160.44	—	—	—
4.0	11.0	.0024	0.020	29	767.49	624.99	386.36	2.40
6.0	17.0	.0108	0.029	30	1577.99	881.17	400.69	2.40
8.0	22.0	.0108	0.035	31	2519.24	1108.75	413.07	2.41
10.0	28.0	.0118	0.041	31	4030.46	1400.16	428.63	2.45
12.0	34.0	.0143	0.046	31	5985.45	1731.01	441.42	2.40

SERIES II : $[try] = 0.02 \text{ M}$ $[Cd^{2+}] = 1.0 \times 10^{-3} \text{ M}$, $\mu = 1.0$ ($NaNO_3$), $pH = 8.2$, Temp. = $25 \pm 0.1^\circ C$



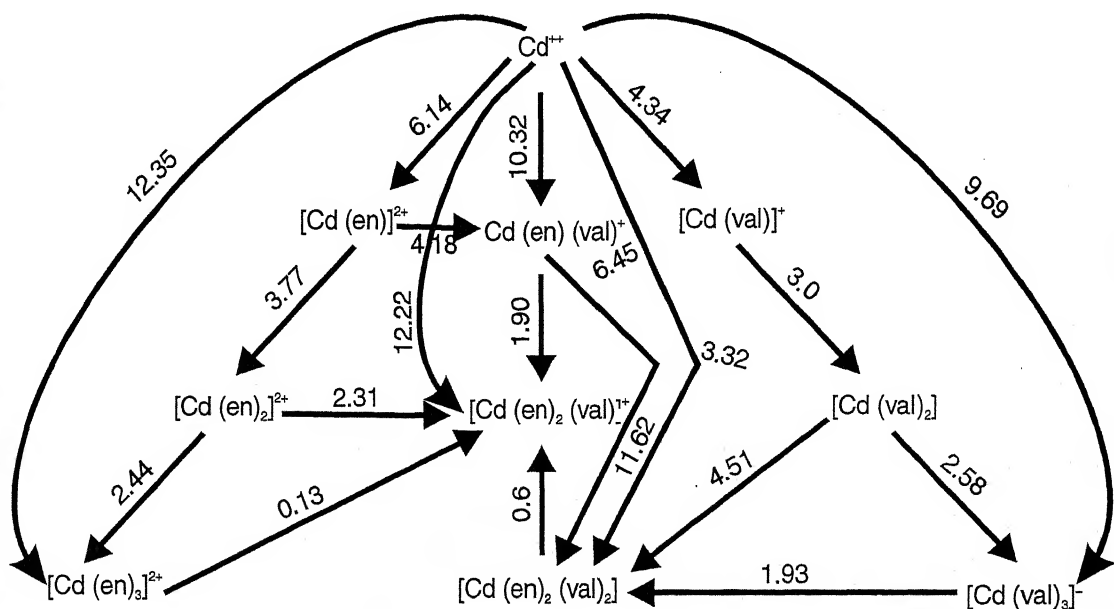
FLWSHEET DIAGRAM - 3.01

CADMIUM - ETHYLENEDIAMINE - GLYCINE SYSTEM



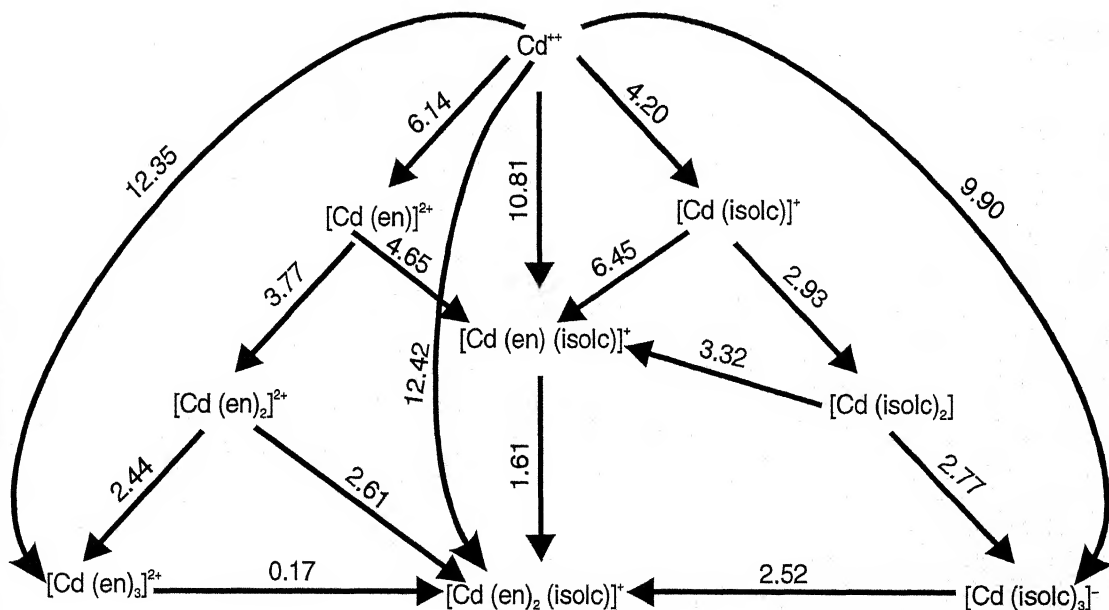
FLWSHEET DIAGRAM - 3.02

CADMIUM - ETHYLENEDIAMINE - ALANINE SYSTEM



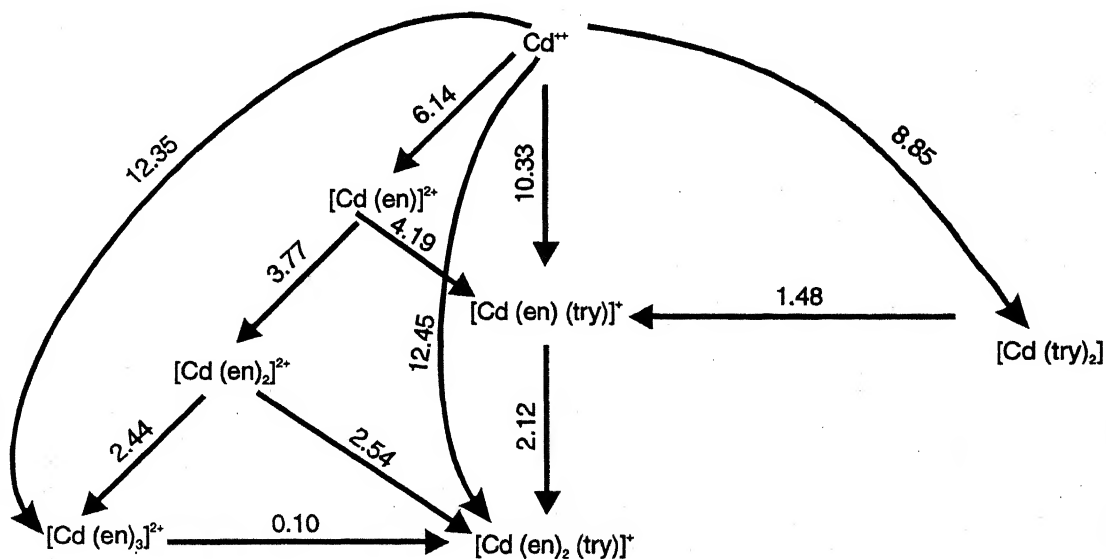
FLWSHEET DIAGRAM - 3.03

CADMIUM - ETHYLENEDIAMINE - VALINE SYSTEM



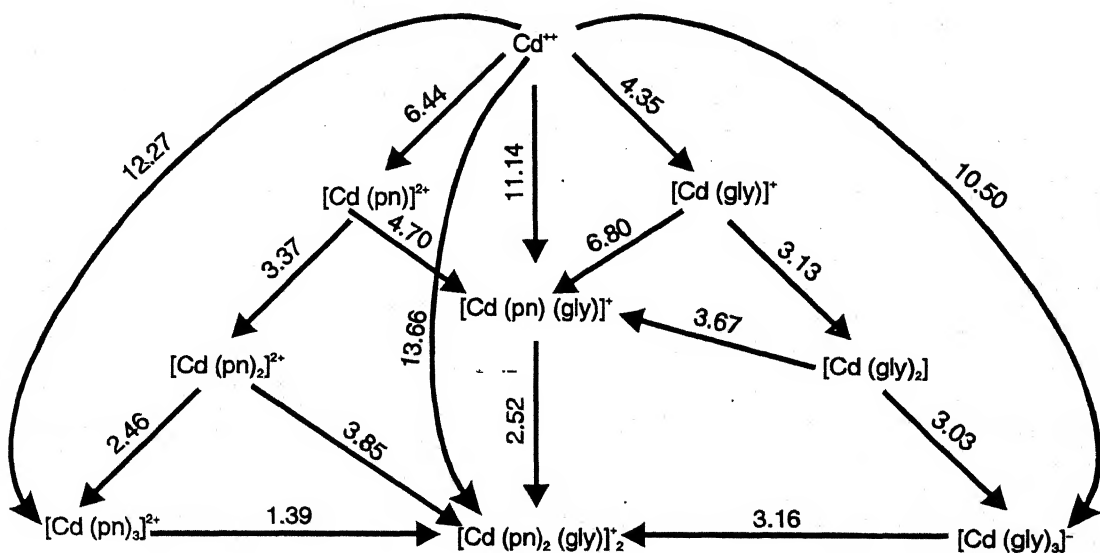
FLWSHEET DIAGRAM - 3.04

CADMIUM - ETHYLENEDIAMINE - ISOLUCINE SYSTEM



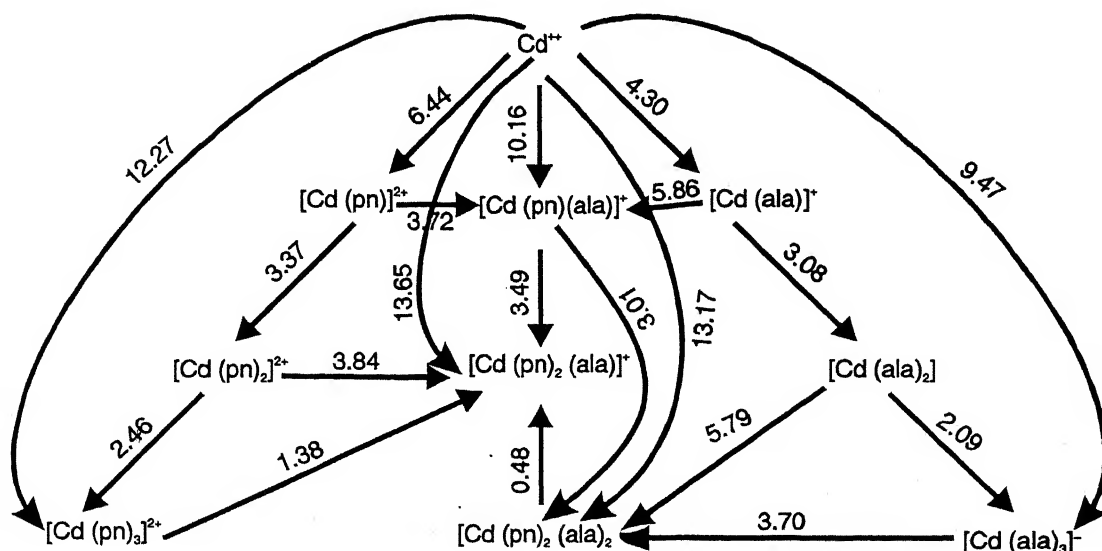
FLWSHEET DIAGRAM - 3.05

CADMIUM - ETHYLENEDIAMINE - TRYPTOPHAN SYSTEM



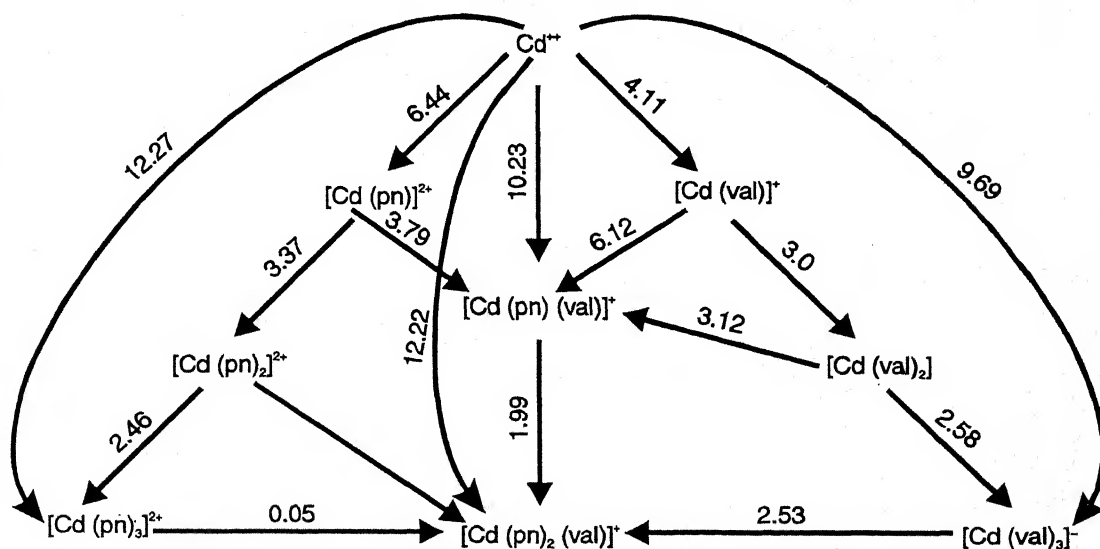
FLWSHEET DIAGRAM - 3.06

CADMIUM - PROPYLENEDIAMINE - GLYCINE SYSTEM



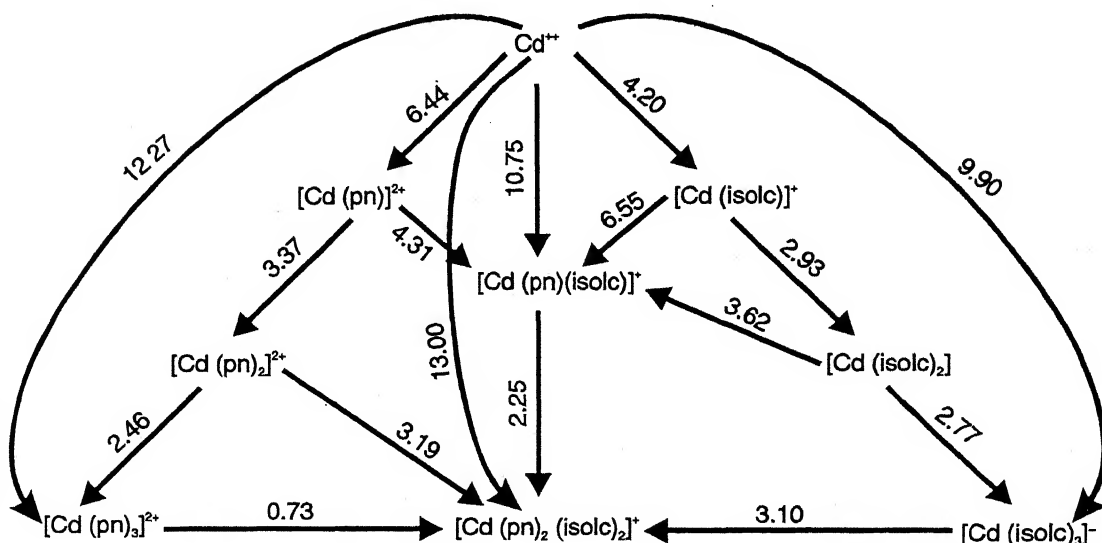
FLWSHEET DIAGRAM - 3.07

CADMIUM - PROPYLENEDIAMINE - ALANINE SYSTEM



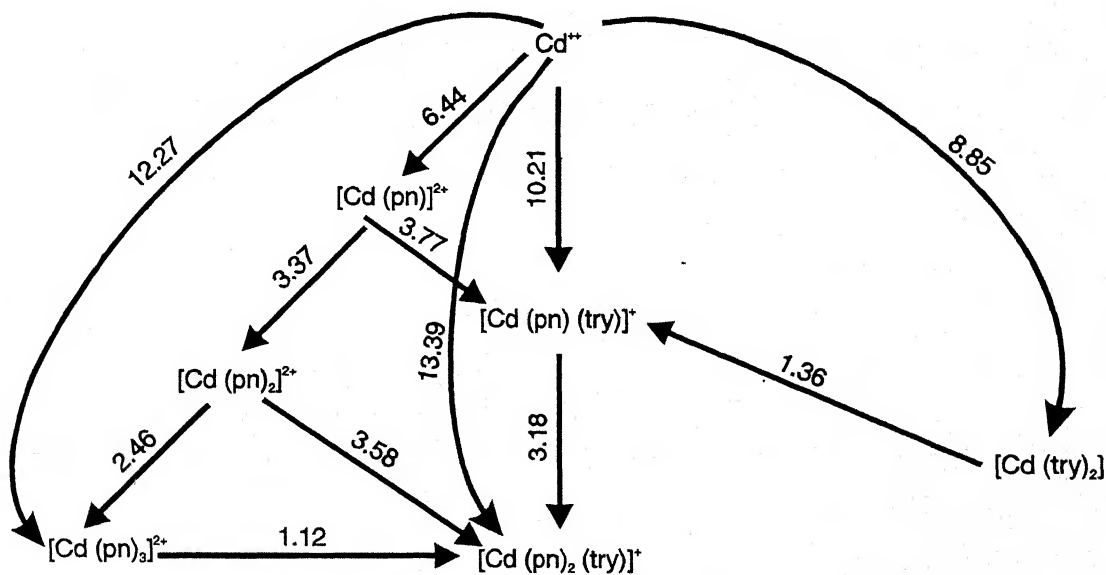
FLWSHEET DIAGRAM - 3.08

CADMIUM - PROPYLENEDIAMINE - VALINE SYSTEM



FLWSHEET DIAGRAM - 3.09

CADMIUM - PROPYLENEDIAMINE - ISOLEUCINE SYSTEM



FLWSHEET DIAGRAM - 3.10

CADMIUM - PROPYLENEDIAMINE - TRYPTOPHAN SYSTEM

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CHAPTER - IV

LEAD

COMPLEXES

4.01 INTRODUCTION :

Pb (II) is known to yield to a well defined polarographic wave which is entirely diffusion controlled and involves two electrons in presence of a number ligands. A number studies on the binary and ternary complex formation by this metal ions are reported in literature. Thus Li and Manning¹ have reported the formation of complexes of lead with cysteine, glutamine histidine and methionine. Similarly multiple 1 : 1 and 1 : 2 complexes formation by Pb (II) ions with glycine has been concluded by Bapna and Karmalkar² on the basis of this reduction at the DME. McKenzie and Mellor³ have, however, observed only 1 : 1 complex formation for the same system. The polarographic behaviour of Pb (II) glutamate system has been studied by Li and Chang⁴ concluding the formation of a number of hydroxy complexes as the higher pH. A comprehensive account of the polarography of Pb (II) complexes with glycine, DL - α - alanine, DL - β - alanine, DL - valine, DL - asparagine, DL - aspartic acid and L - glutamic acid has been provided by Rao and Subramanya⁵⁻⁸. A number of such studies⁹⁻¹³ on binary systems of Pb (II) have been reported.

Kim et al¹⁴ have in reported the formation ternary complexes of Pb (II) with histidine and hydroxide ions in the higher pH range. A series of studies have been undertaken by Garg and co-workers¹⁵⁻²¹ on the Pb (II) complexes with some carboxylic acids and ethylenediamine and propylenediamine. Saxena and co-workers²²⁻²³ have carried out polarography of Pb (II) with amino acid as the primary ligands and pyridoxine and ascorbic acid as secondary ligands. There is also a study of Saxena et al²⁴ on the polarography of ternary complex formation by the metal ion with

pyridoxine and amino acids. Similarly, there are other reports²⁵⁻²⁹ of investigations on mixed ligand complex formation by lead ion.

In this chapter we have reported the results of polarographic studies of ternary complexes of the metal ion with ethylenediamine (en) and propylenediamine (pn) separately as the primary ligands which are displaced respectively by amino acids such as glycine (gly), DL - alanine (ala), DL - valine (val), L - isoleucine (isoleu) and L - tryptophan (try). In the simple as well as the mixed systems, Pb (II) continues to yield well defined two electron reduction waves of a diffusion controlled nature. All the studies were carried out at a pH of 6.0 with ionic strength kept constant at 1.0 M. by adding varying amounts of NaNO₃ at 25 ± 0.1°C. In each case lead has been found to form only one 1 : 1 : 1 complex. The following mixed systems have been investigated.

- | | | | | | |
|-----|---------|---|------------------|---|----------------|
| (a) | Pb (II) | - | ethylenediamine | - | glycine |
| (b) | Pb (II) | - | ethylenediamine | - | DL - alanine |
| (c) | Pb (II) | - | ethylenediamine | - | DL - valine |
| (d) | Pb (II) | - | ethylenediamine | - | L - isoleucine |
| (e) | Pb (II) | - | ethylenediamine | - | L - tryptophan |
| (f) | Pb (II) | - | propylenediamine | - | glycine |
| (g) | Pb (II) | - | propylenediamine | - | DL - alanine |
| (h) | Pb (II) | - | propylenediamine | - | DL - valine |
| (i) | Pb (II) | - | propylenediamine | - | L - isoleucine |
| (j) | Pb (II) | - | propylenediamine | - | L - tryptophan |

4.02 EXPERIMENTAL

Only the analytical reagent grade chemicals were used and only

doubled distilled water was used to prepare and dilute solutions. Sodium nitrate was used to maintain ionic strength constant at 1.0 M. Triton X - 100 ($2 \times 10^{-3}\%$) was added to every test solution as maxima was observed for the systems under investigations. As described in chapter II, the concentration of the ligand was increased while keeping the ionic strength and pH constant. The polarograms of the test solutions were recorded. All measurements were made at $25 \pm 0.1^\circ\text{C}$. All recorded current and potential values were corrected for residual current and iR drop of the cell respectively. Capillary characteristics of the DME were as follows :

$$m = 2.40 \text{ mg/sec}, \quad t = 3.10 \text{ sec.}, \quad \text{at } h_{\text{corr.}} = 52.4 \text{ cm.}$$

The pH of test solutions was adjusted by adding requisite amounts of dilute NaOH or HCl using a Toshniwal, CL - 49 pH meter.

n , the number of electrons involved in the reduction at DME of Pb (II) in presence of different ligands was determined as already described³⁰ in chapter II. In each and every case, the value of n was found to be 2.

4.03. RESULTS AND DISCUSIONS

4.03.01 DETERMINATION OF pKa VALUES

The determination of pKa values of the ligands was carried out as already described in chapter III.

Table 4.01 to 4.17 contain the experimental data for the simple and ternary complex system of Pb (II).

4.03.02 NATURE OF POLAROGRAPHIC WAVES

In each and every case Pb (II) gave a well defined polarographic wave in varying concentration of ethylene diamine (en), propylenediamine (pn), glycine (gly), DL - alanine (ala), DL - valine (val), L - isoleucine

(isolec), and L - tryptophan (try) present singly or in combination. In each case the reduction was found to be entirely diffusion controlled as borne out by the linear nature of i_d vs $h_{corr}^{1/2}$ plots and their passing through the origin.

The reduction in each case was also found to be reversible - an inference³¹ drawn from the linearity of plots of $\log i/i_d - i$ vs $E_{d.e.}$ with slopes of the order of 31 ± 2 mV.

4.03.03 COMPOSITION AND STABILITY OF SIMPLE COMPLEX

It was deemed essential to determine the composition and stability constants of simple complexes of Pb (II) with ethylenediamine (en), propylenediamine (pn), glycine (gly), DL - alanine (ala), DL - valine (val), L - isoleucine (isolec) and L - tryptophan (try) separately before mixed ligand complexes were investigated. However, identical conditions were maintained for both simple and mixed complex systems.

Solutions containing 1.0×10^{-3} M Pb (II), 0.1 M en and also 1.0×10^{-3} M Pb (II) with 0.1 M pn 0.002% triton - X - 100 and ionic strength of 1.0 (NaNO_3) were polarographically examined at varying pH. There was a perceptible change in $E_{1/2}$ with change in pH. It was observed that $E_{1/2}$ was maximum at pH 6.0 for both the ligands. It was for this reason that this pH was selected to study the simple as well as mixed complexes. Obviously OH^- ions are unable to compete with en and pn to enter the coordination sphere.

Table 4.01 to 4.07 contain the polarographic data of simple Pb (II) - en, Pb (II) - pn, Pb (II) - gly, Pb (II) - ala, Pb (II) - val, Pb (II) - isolec, and Pb (II) - try systems. In each case, there is a cathodic shift

as well as decrease in diffusion current with increase in ligand concentration. It indicates complex formation. Except in the case of Pb (II - ala), and Pb (II) - try system, the plot of $\log [\text{ligand}]$ vs $E_{1/2}$ are smooth curves indicating successive complex formation. Hence the method of DeFord and Hume³² was applied to determine the stability of two successive complexes in each case (Table - 4.01 to 4.07 and figures 4.08 to 4.18 except figure 4.14).

In the case of Pb (II) - ala and Pb (II) - try complexes, however, the $\log [\text{ala}]$ and $\log [\text{try}]$ vs $E_{1/2}$ plots yield a straight lines [Fig. 4.14 and 4.19]. Hence formation of only one complex was concluded in each case. Its composition and stability was determined by Lingane's method³³.

The composition and stability constants of complexes so obtained are summarised below

System	Compositon	Stability Constant	
		$\log \beta_1$	$\log \beta_2$
Pb (II) - en	1 : 1, 1 : 2	7.32	13.47
Pb (II) - pn	1 : 1, 1 : 2	7.11	12.77
Pb (II) - gly	1 : 1, 1 : 2	5.27	9.62
Pb (II) - ala	____, 1 : 2	____	9.40
Pb (II) - val	1 : 1, 1 : 2	5.14	9.46
Pb (II) - isolc	1 : 1, 1 : 2	5.17	9.39
Pb (II) - try	____, 1 : 2	____	8.32

4.03.04 COMPOSITION AND STABILITY OF MIXED COMPLEXES

In order to determine the composition and stability constants of mixed ligand complexes a ligand displacement techniques was used and

the method of Schaap and McMasters³⁴ applied. In these mixed ligand systems too, the reduction was found to be reversible involving 2 electrons and entirely diffusion controlled. (Figure 4.20 to 4.29)

(A) Pb (II) - ETHYLENEDIAMINE - GLYCINE SYSTEM

In the system, [gly] was kept constant at 0.2 M and that of ethylene diamine varied from 0 to 0.10 M. Polarography of such solution revealed that $E_{1/2}$ exhibits greater cathodic shift³⁵ than that in absence of glycine (Table 4.01 and 4.08). It indicated mixed ligand complex formation by glycinate ion and ethylenediamine with Pb (II), ion. The procedure was repeated at [gly] = 0.3 M. The polarographic data at the two fixed concentration of [gly] is presented in table 4.08. From the plots (Figure 4.30) of F_{ij} vs [en], the value of the constants^{34,36} obtained is as follows

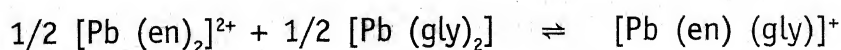
	log A	log B	log C
At [gly] = 0.2 M	0.77	7.43	13.64
At [gly] = 0.3 M	0.90	7.54	13.69

From the values of A, B and C the mixed complex stability constant value was calculated to be

$$\beta_{11} = \log 11.68 \text{ for } [\text{pb}(\text{en})(\text{gly})]$$

Flowsheet diagram 4.01 conveniently summarises results obtained for logarithms of equilibrium constant of the reactions indicated by the arrow.

The mixing constant (K_M) for the reaction



can be calculated from the following relation

$$\log K_M = \log \beta_{11} - 1/2 (\log \beta_{20} + \log \beta_{02})$$

In the present system the $\log K_M$ value has been found to be + 0.13 indicating that the mixed 1 : 1 : 1 complex is more stable than the two binary 1 : 2 complexes.

In the following disproportionation reaction⁵



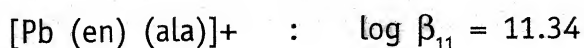
The equilibrium constant has been found to be - 0.27. It once again shows that ternary complexes are much stronger than binary complexes for the metal ion the ligands under investigation.

(B) Pb (II) - ETHYLENEDIAMINE - DL - ALANINE SYSTEM

In this system, the concentration of ethylenediamine varied from 0.0 to 0.10 M keeping [ala] constant at 0.2 and 0.3 M respectively for the obtaining two sets of $E_{1/2}$ and i_d data. A greater cathodic shift of $E_{1/2}$ in presence of alanine was noted for each concentration of ethylenediamine in both the series indicating mixed ligand complex formation between Pb^{++} ion of the one hand and ethylenediamine and alanine on the other (Table 4.01 and 4.09). Two sets of F_{ij} [X,Y] obtained from experimental values yield two sets of values of A, B and C. (as illustrated in fig. 4.31)

[ala]	$\log A$	$\log B$	$\log C$
0.2 M	0.60	7.59	13.49
0.3 M	0.69	7.62	13.49

The only mixed ligand complex formed had the following composition and stability



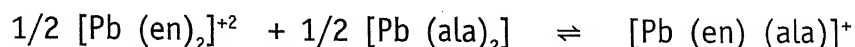
This result broken up into various equilibria is represented in flowsheet diagram 4.02. The numerical figures stand for the logarithm

values of equilibrium constants of the reaction involved.

The equation

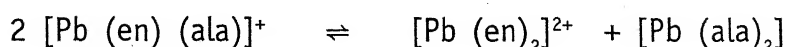
$$\log K_M = \log \beta_{11} - 1/2 (\log \beta_{20} + \log \beta_{02})$$

can be used to evaluate the mixing constant K_M of the equilibrium.



It has been found to be - 0.09 for the system. A negative value of K_M is indicative of less stability of the mixed complex $[\text{Pb} (\text{en}) (\text{ala})]^+$ over simple $[\text{Pb} (\text{en})_2]^{2+}$ and $[\text{Pb} (\text{ala})_2]$ complexes.

For the following disproportionation reaction.



The equilibrium constant is + 0.19. The positive values are once again suggestive of less stability of mixed ligand complex over simple binary complexes.

(C) Pb (II) - ETHYLENEDIAMINE - DL - VALINE SYSTEM

Keeping the concentration of valine constant at 0.2 M and 0.3 M respectively and varying the concentration of ethylenediamine from 0.00 to 0.1 M, two series of polarographic data were obtained. It was noted that the cathodic shift in $E_{1/2}$ of Pb^{++} ion in presence of valine was greater than that in its absence at each concentration of ethylenediamine (Table - 4.01 and 4.10). Inferring mixed complex formation, the $F_{ij} [X,Y]$ functions were determined and values of constants A, B and C obtained for both series (figure 4.32).

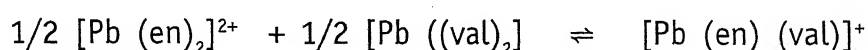
[val]	log A	log B	log C
0.2 M	0.65	7.59	13.47
0.3 M	0.69	7.62	13.49

Consequently the stability constant of mixed complex was evaluated



The flowsheet diagram 4.03 gives a graphic account of various complex species existing in the solution and their relative stability. The numerical figures represent the logarithm of equilibrium constant of the reaction indicated by the concerned arrow mark.

The mixing constant K_M for the reaction



can be computed from the equation

$$\log K_M = \log \beta_{11} - 1/2 (\log \beta_{20} + \log \beta_{02})$$

The numerical value of K_M for the system has been found to be - 0.27. Decisively, therefore, the ternary 1 : 1 : 1 complex is less stable than the parent 1 : 2 binary complex.

Similar results are obtained from the disproportionation constants of the following reaction.



The constant is 0.55. The positive value is once again suggestive that formation of ternary complexes is not favoured over binary simple complex.

(D) Pb (II) - ETHYLENEDIAMINE - L - ISOLEUCINE SYSTEM

In this system, the concentration of ethylenediamine was varied from 0.00 to 0.10 M keeping [isoleucine] constant at 0.2 M and 0.3 M respectively for the obtaining two sets of $E_{1/2}$ and i_d data. A greater cathodic shift in $E_{1/2}$ in presence of isoleucine was noted for each concentration of

ethylenediamine in both the series indicating mixed ligand complex formation between Pb^{++} ion on the one hand and ethylenediamine and isoleucine on the other (Table 4.01 and 4.11).

Two sets of F_{ij} [X,Y] data obtained from experimental values yield two sets of values of A, B and C from figure 4.33.

[Isolc]	log A	log B	log C
0.2 M	0.95	7.52	13.46
0.3 M	1.00	7.59	13.47

The only mixed ligand complex formed had the following composition and stability

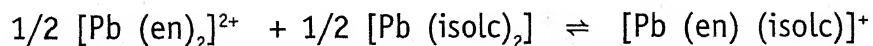


This result broken up into various equilibria is represented in flowsheet Diagram 4.04. The numerical values stand for the logarithm value of equilibrium constant of the reaction involved.

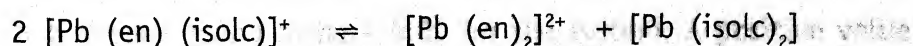
The equation

$$\log K_M = \log \beta_{11} - 1/2 (\log \beta_{20} + \log \beta_{02})$$

can be used to evaluate the mixing constant K_M of the equilibrium



It has been found to be + 0.16 for the system. A positive value of K_M is indicative of greater stability of the mixed complex $[Pb (en) (isolc)]^+$ over simple $[Pb (en)_2]^{2+}$ and $[Pb (isolc)_2]$ complexes for the following disproportionation reaction



Its equilibrium constant is - 0.32. The large negative value is the once again suggestive of greater stability of mixed ligand complex over

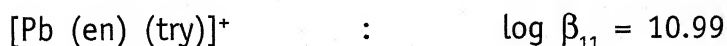
simple binary complex.

(E) Pb (II) - ETHYLENEDIAMINE - L - TRYPTOPHAN SYSTEM

During the investigation of mixed ligand formation in this system, the [try] was kept constant at 0.2 M to 0.3 M respectively while concentration of ethylenediamine increased from 0.00 to 0.10 M in both the series. The half wave potential value exhibited a greater cathodic shift in presence of tryptophan than that in each case at each for [en] only (Table 4.01 and 4.12). It indicated complex formation of Pb (II) with ethylenediamine and tryptophan. The computations at the two concentration of tryptophan (Table 4.12) lead to the constants A, B and C as shown in figure 4.34).

[try]	log A	log B	log C
0.2 M	0.69	7.49	13.55
0.3 M	0.69	7.54	13.55

The only mixed ligand complex formed had the following composition and stability.

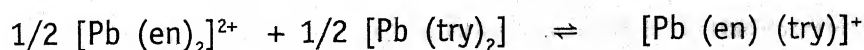


This result broken up into various equilibrium is represented in flowsheet diagram 4.05.

The equation

$$\log K_M = \log \beta_{11} - 1/2 (\log \beta_{20} + \log \beta_{02})$$

can be used to evaluate the mixing constant K_M of the equilibrium.



It has been found to be + 0.09 for the system. A positive value of K_M is indicative of greater stability of the mixed complex $[\text{Pb (en) (try)}]^+$ over simple $[\text{Pb (en)}_2]^{2+}$ and $[\text{Pb (try)}_2]$ complexes.

For the following disproportionation reaction



The equilibrium constant at - 0.19. The negative value is once again suggestive of greater stability of mixed ligand complex over simple binary complex.

(F) Pb (II) - PROPYLENEDIAMINE - GLYCINE SYSTEM

During the investigation of mixed ligand formation in this system, the [gly] was kept constant at 0.2 M to 0.3 M respectively while concentration of propylenediamine increases from 0.00 to 0.1 M in both the series. The half wave potential values exhibited a greater cathodic shift in presence of glycine than that in absence glycine each case at each [pn] (Table 4.02 and 4.13). It indicated complex formation of Pb (II) with propylenediamine and Glycine. The computation of Glycine of F_{ij} [X,Y] functions at the two concentrations of glycine (Table 4.13) lead to the calculation of constants A, B and C as depicted in figure 4.35.

[gly]	log A	log B	log C
0.2 M	0.69	7.25	12.78
0.3 M	0.77	7.39	12.78

The only mixed ligand complex formed had the following composition and stability.

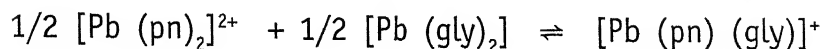


This results broken up into various equilibria is represented in flowsheet diagram 4.06. The numerical figures stand for the logarithm values of equilibrium constant of the reaction involved.

The equation

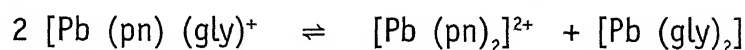
$$\log K_M = \log \beta_{11} - 1/2 (\log \beta_{20} + \log \beta_{02})$$

can be used to evaluate the mixing constant K_M of the equilibrium



It has been found to be + 0.42 for the system. A positive value of K_M is indicative of greater stability of mixed complex $[\text{Pb (pn) (gly)}]^+$ over simple $[\text{Pb (pn)}_2]^{2+}$ and $[\text{Pb (gly)}_2]$ complexes.

For the following disproportionation reaction



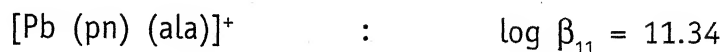
the equilibrium constant is - 0.85. The negative value is once again suggestive of greater stability of mixed ligand complex over simple binary complexes.

[G] Pb (II) - PROPYLENEDIAMINE - DL - ALANINE SYSTEM

During the investigation of mixed ligand formation in this system, the $[\text{ala}]$ was kept constant at 0.2 M and 0.3 M respectively while concentration of propylenediamine increased from 0 to 0.10 M in both the series. The half wave potential values exhibited a greater cathodic shift in presence of alanine than that in its absence each case at each $[\text{pn}]$ (Table 4.02 and 4.13). It indicated complex formation of Pb (II) with propylenediamine and alanine. The computation of values of F_{ij} $[X,Y]$ functions at the concentration of alanine (Table 4.13) lead to the calculation of the constants A, B and C (figure 4.36.)

$[\text{ala}]$	$\log A$	$\log B$	$\log C$
0.2 M	0.84	7.36	12.76
0.3 M	0.84	7.41	12.78

The only mixed ligand complex formed had the following composition and stability.

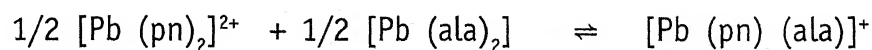


This result broken up into various equilibria is represented in flowsheet Diagram 4.07. The numerical figures stand for the logarithm values of equilibrium constant of the reaction involved.

The equation

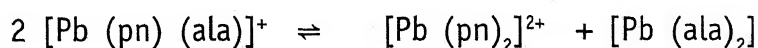
$$\log K_M = \log \beta_{11} - 1/2 (\log \beta_{20} + \log \beta_{02})$$

can be used to evaluate the mixing constant K_M of the equilibrium



It has been found to be + 0.25 for the system. A positive value of K_M is indicative of greater stability of the mixed complex $[\text{Pb (pn) (ala)}]^+$ over the simple $[\text{Pb (pn)}_2]^{2+}$ and $[\text{Pb (ala)}_2]$ complexes.

For the following disproportionation reaction



The equilibrium constant is - 0.51. The negative value is once again suggestive of greater stability of mixed ligand complex over simple binary complexes.

(H) Pb (II) - PROPYLENEDIAMINE - DL - VALINE SYSTEM

During the investigation of mixed ligand formation in this system, the [val] was kept constant at 0.02 and 0.3 M respectively while concentration of propylenediamine increased from 0.0 to 0.10 M in both the series. The half wave potential values exhibited a greater cathodic shift in presence of valine than that in its absence each case at each [pn] (Table 4.02 and 4.15). It indicated complex formation of Pb (II) with

propylenediamine and valine. The computation of values of F_{ij} [X,Y] functions at the two concentrations of valine (Table 4.15) lead to the calculation of the constant A, B and C (as per figure 4.37).

[val]	log A	log B	log C
0.2 M	0.84	7.34	12.77
0.3 M	0.84	7.44	12.77

The only mixed ligand complex formed had the following composition and stability

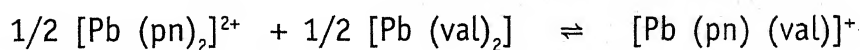
$$[\text{Pb (pn) (val)}]^+ : \log \beta_{11} = 11.49$$

This result broken up into various equilibria is represented in flowsheet Diagram 4.08. The numerical figures stand for the logarithm of equilibria involved.

The equation

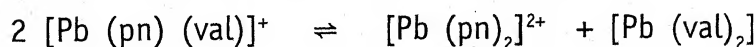
$$\log K_M = \log \beta_{11} - 1/2 (\log \beta_{20} + \log \beta_{02})$$

can be used to evaluate the mixing constant K_M of the equilibrium.



it has been found to + 0.37 for the system. A positive value of K_M is indicative of greater stability of the mixed complex $[\text{Pb (pn) (val)}]^+$ over simple $[\text{Pb (pn)}_2]^{2+}$ and $[\text{Pb (val)}_2]$ complexes.

For the following disproportionation reaction



the equilibrium constant is - 0.75. The negative value is once again suggestive of greater stability of mixed ligand complex over simple binary complexes.

(I) Pb (II) - PROPYLENEDIAMINE - L - ISOLEUCINE SYSTEM

During the investigation of mixed ligand formation in this system, the (isolc) was kept constant at 0.2 and 0.3 M respectively while concentration of propylenediamine increase from 0 to 0.10 M in both the series. The half wave potential values exhibited a greater cathodic shift in presence of isoleucine than that in its absence in each case at each [pn] (Table 4.02 and 4.16). It indicated complex formation of Pb (II) with propylenediamine and isoleucine. The computation of values of F_{ij} [X,Y] functions at different concentrations of isoleucine (table 4.16) lead to the calculation of the constants A, B and C (vide figure 4.38).

[isolc]	log A	log B	log C
0.2 M	0.84	7.46	12.75
0.3 M	0.90	7.49	12.76

The only mixed ligand complex formed had the following composition and stability

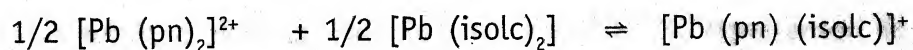
$$[\text{Pb (pn) (isolc)}]^+ : \log \beta_{11} = 11.05$$

This result broken up into various equilibria is represented in flowsheet Diagram 4.09. The numerical figures stand for the logarithm values of equilibria constants of reactions involved.

The equation

$$\log K_M = \log \beta_{11} - 1/2 (\log \beta_{20} + \log \beta_{02})$$

can be used to evaluate the mixing constant K_M of the equilibrium



It has been found to be - 0.03 for the system. A negative value of K_M is indicative of less stability of mixed complex $[\text{Pb (pn) (isolc)}]^+$ over

simple $[\text{Pb}(\text{pn})_2]^{2+}$ and $[\text{Pb}(\text{isolc})_2]$ complexes.

For the following disproportionation reaction.



In equilibrium constant is + 0.06. The positive value is once again suggestive of less stability of mixed ligand complex over simple binary complexes.

(J) Pb (II) - PROPYLENEDIAMINE - L - TRYPTOPHAN SYSTEM

During the investigation of mixed ligand formation in this system, the $[\text{try}]$ was kept constant at 0.2 M and 0.3 M respectively while concentration of propylenediamine increases from 0.0 to 0.10 M in both the series. The half wave potential values exhibited a greater cathodic shift in presence of tryptophan than that in its absence in each case at each $[\text{pn}]$ (Table 4.02 and 4.17). It indicated complex formation of Pb (II) with propylene diamine and tryptophan. The computation of values of F_{ij} $[X,Y]$ functions at the two concentrations of tryptophan lead to the constants A, B and C (vide figure 4.39).

$[\text{try}]$	$\log A$	$\log B$	$\log C$
0.2 M	0.77	7.30	12.79
0.3 M	0.84	7.38	12.82

The one mixed ligand complex formed had the following composition and stability

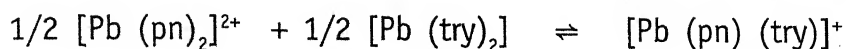


This result broken up into various equilibria is represented in flowsheet Diagram 4.10. The numerical figures stand for the logarithm values of equilibrium constants of reactions involved.

The equation

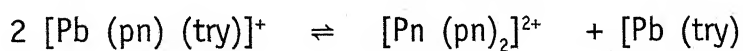
$$\log K_M = \log \beta_{11} - 1/2 (\log \beta_{20} + \log \beta_{02})$$

can be used to evaluate the mixing constant K_M of the equilibrium.



It has been found to be + 0.44 for the system. A positive value of K_M is indicative of greater stability of the mixed complex $[\text{Pb (pn) (try)}]^+$ over simple $[\text{Pb (pn)}_2]^{2+}$ and $[\text{Pb (try)}_2]$ complex.

For the following disproportionation reaction



The equilibrium constant is - 0.89. The negative value is once again suggestive of greater stability of mixed ligand complex over simple binary complexes.

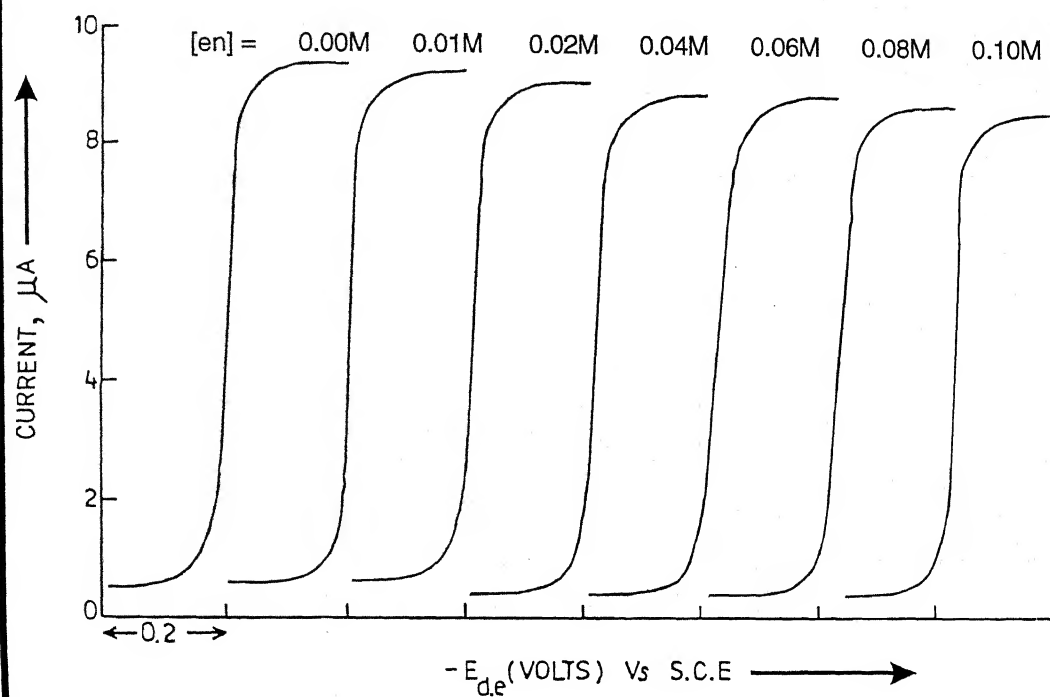


FIG. 4.01 POLAROGRAPHIC WAVES OF Pb (II) - ETHYLENEDIAMINE SYSTEM

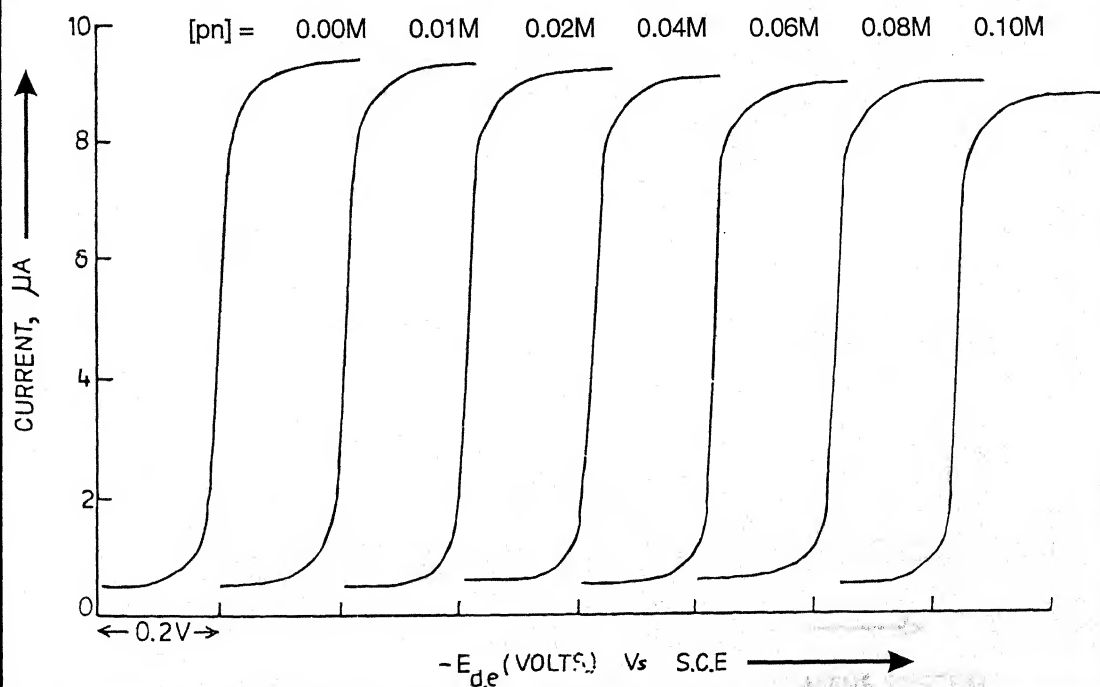


FIG. 4.02 POLAROGRAPHIC WAVES OF Pb (II) - PROPYLENEDIAMINE SYSTEM

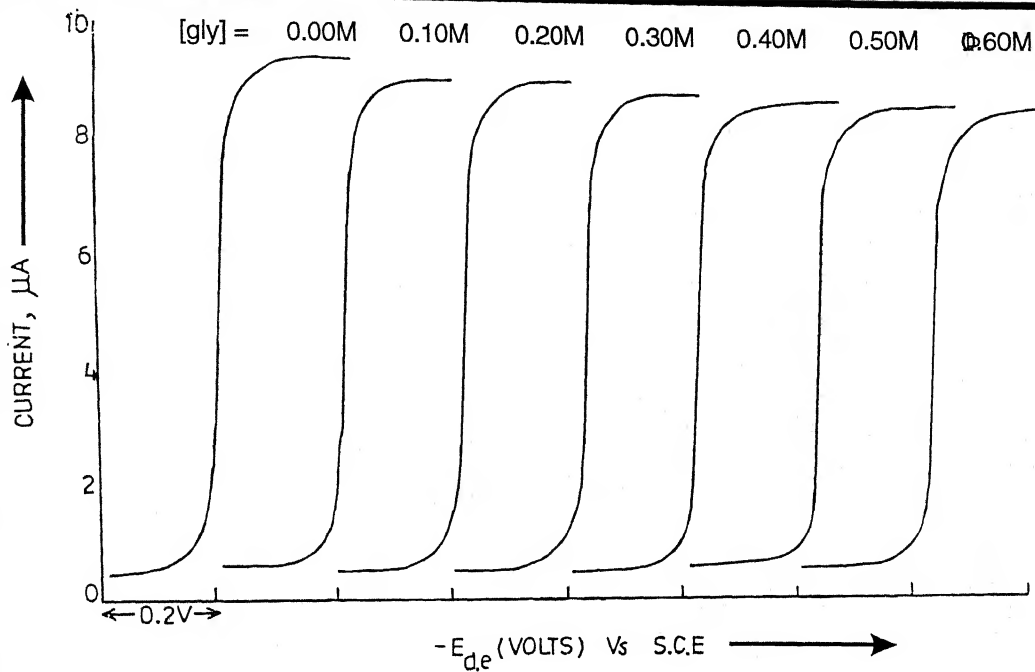


FIG. 4.03 POLAROGRAPHIC WAVES OF Pb (II) - GLYCINE SYSTEM

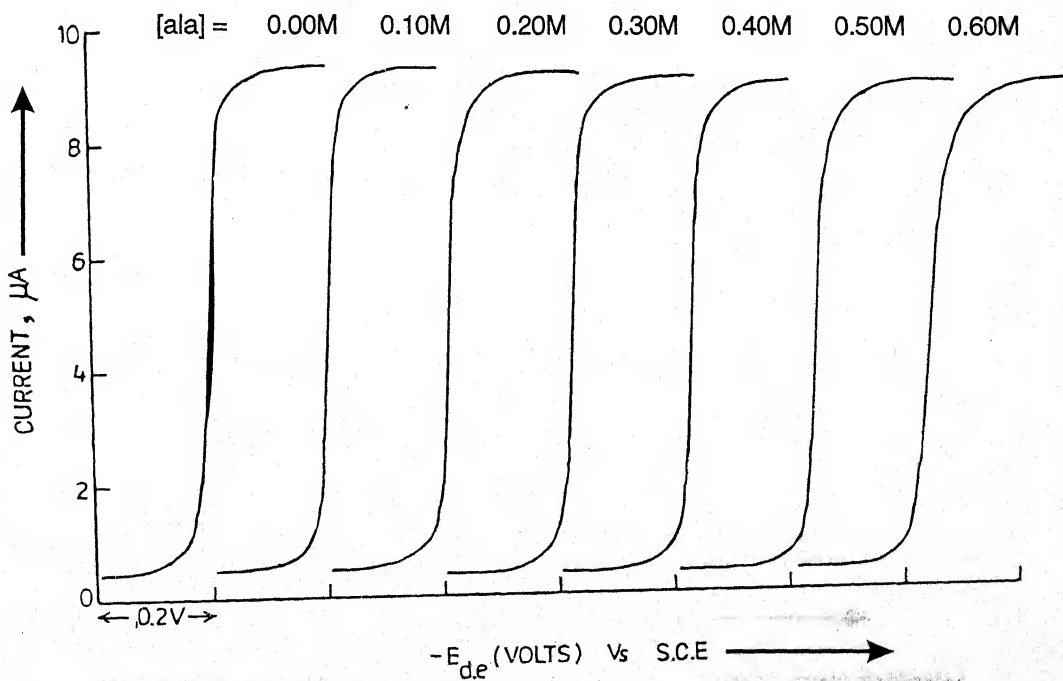


FIG. 4.04 POLAROGRAPHIC WAVES OF Pb (II) - DL - ALANINE SYSTEM

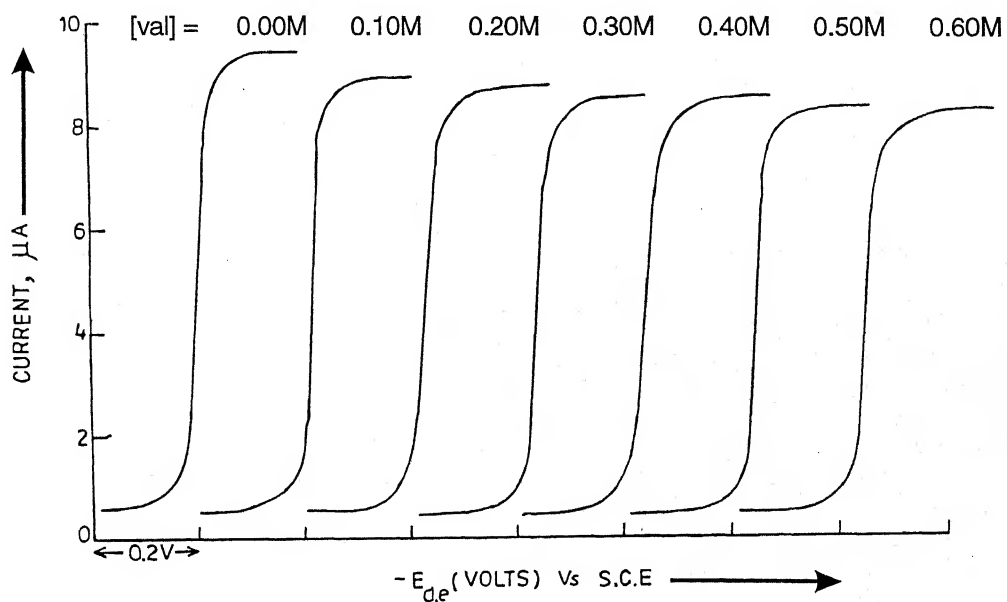


FIG. 4.05 POLAROGRAPHIC WAVES OF Pb (II) - DL - VALINE SYSTEM

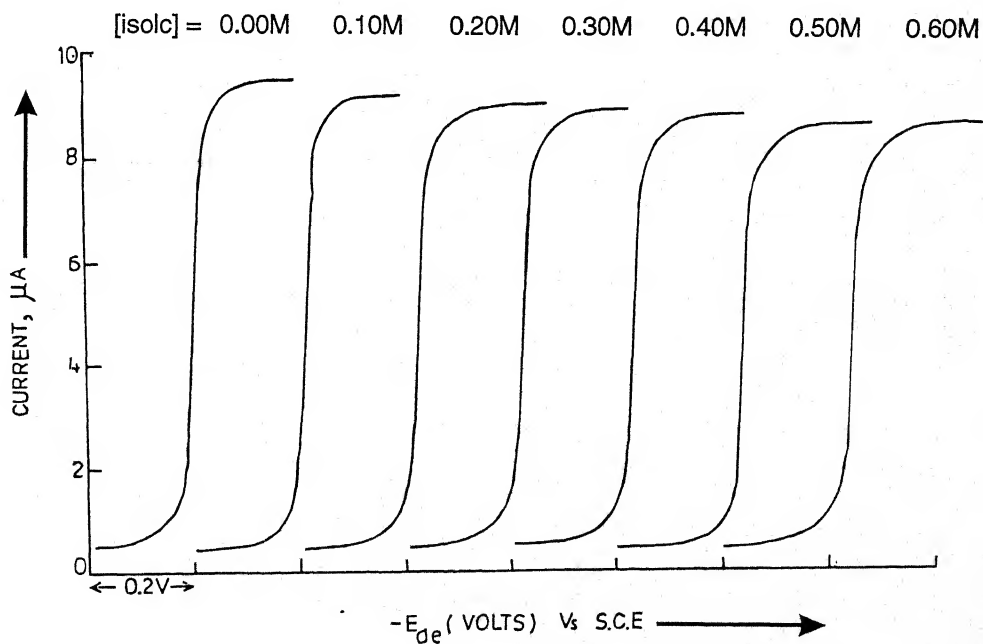


FIG. 4.06 POLAROGRAPHIC WAVES OF Pb (II) - L - ISOLEUCINE SYSTEM

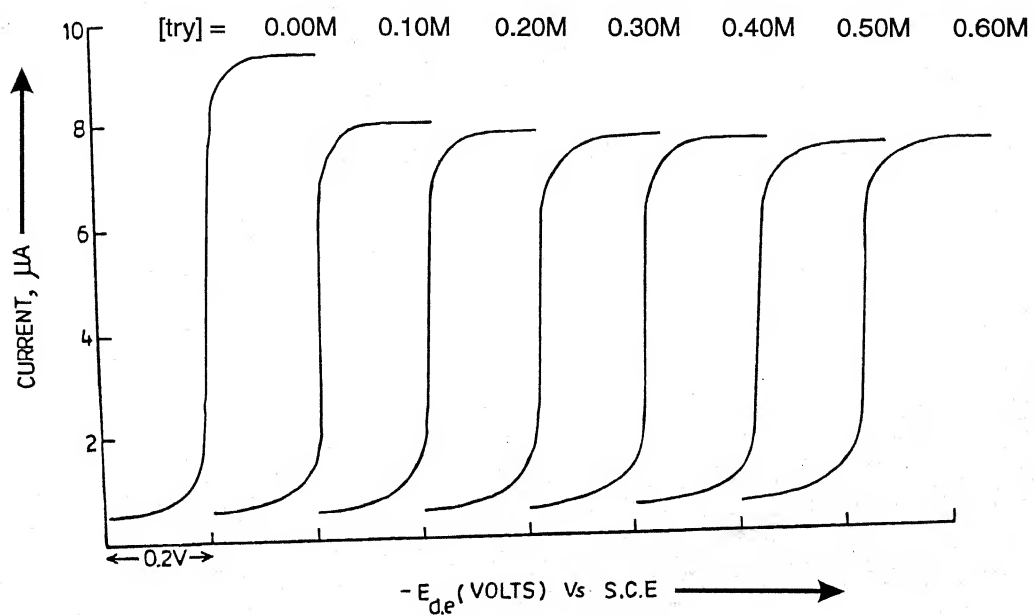


FIG. 4.07 POLAROGRAPHIC WAVES OF Pb (II) - L - TRYPTOPHAN SYSTEM

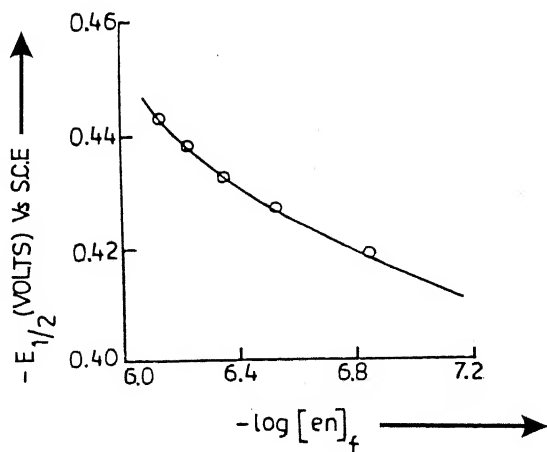


FIG. 4.08 PLOT OF $-E_{1/2}$ Vs $-\log [en]_f$ FOR Pb (II) - ETHYLENEDIAMINE SYSTEM

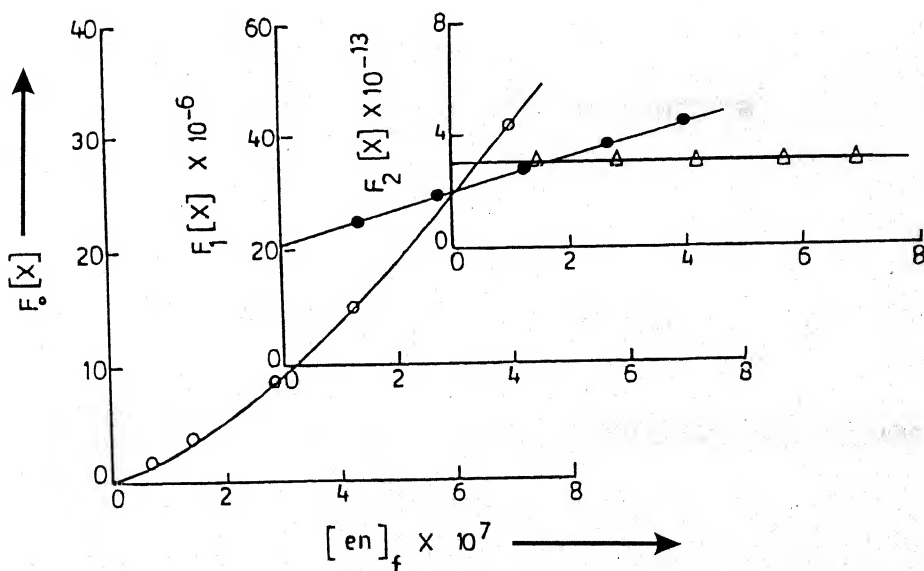


FIG. 4.09 PLOT OF $F_1[X]$ Vs $[en]_f$ FOR Pb (II) - ETHYLENEDIAMINE SYSTEM

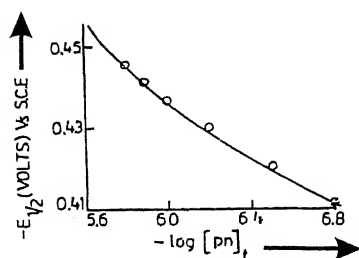


FIG. 4.10 PLOT OF $-E_{1/2}$ Vs $-\log [pn]_f$ FOR Pb (II) - PROPYLENEDIAMINE SYSTEM

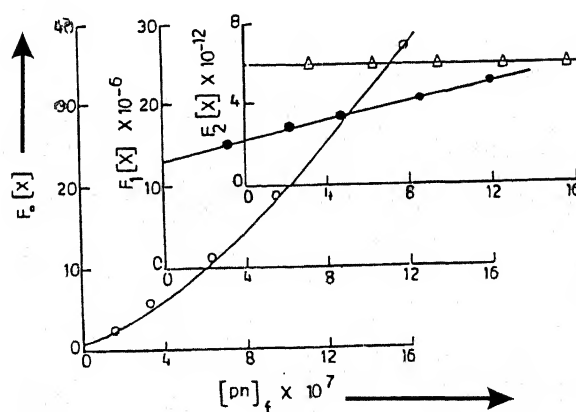


FIG. 4.11 PLOT OF $F_1 [X]$ Vs $[pn]_f$ FOR Pb (II) - PROPYLENEDIAMINE SYSTEM

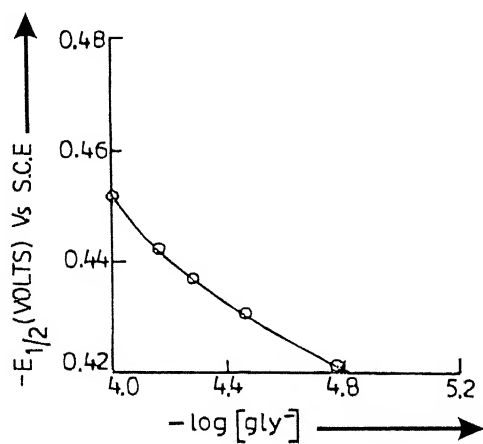


FIG. 4.12 PLOT OF $-E_{1/2}$ Vs $-\log [\text{gly}]$ FOR Pb (II) - GLYCINE SYSTEM

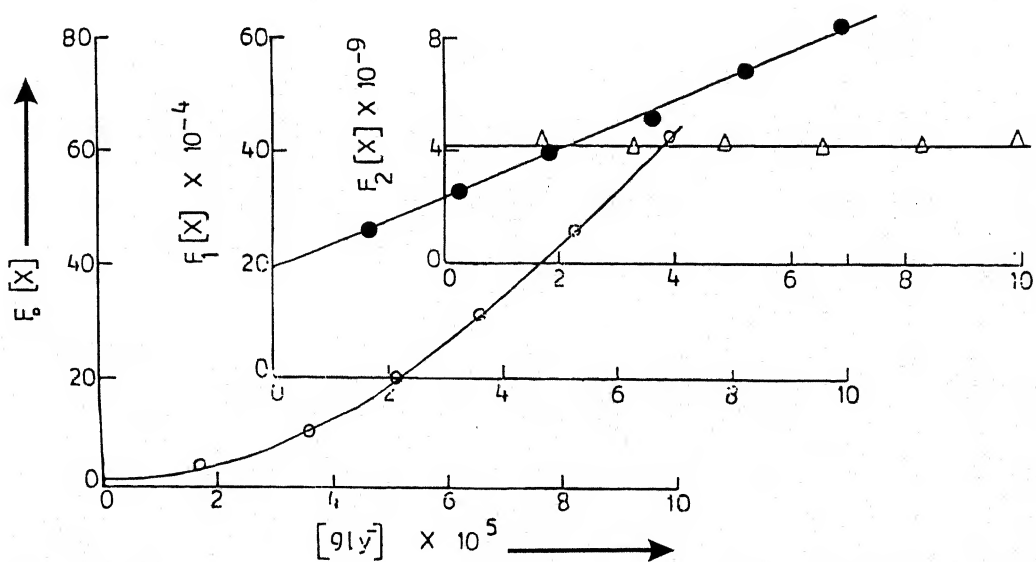


FIG. 4.13 PLOT OF $F_1 [X]$ Vs $[\text{gly}]$ FOR Pb (II) - GLYCINE SYSTEM

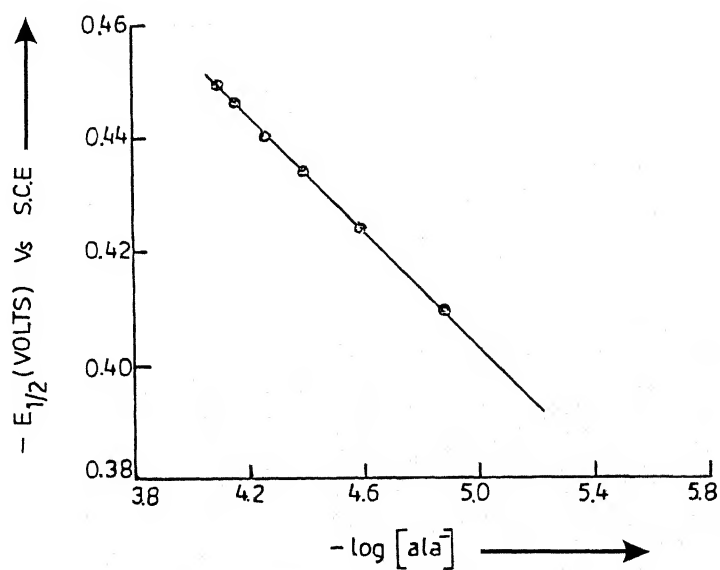


FIG. 4.14 PLOT OF $-E_{1/2}$ Vs $-\log [\text{ala}]$ FOR Pb (II) - ALANINE SYSTEM

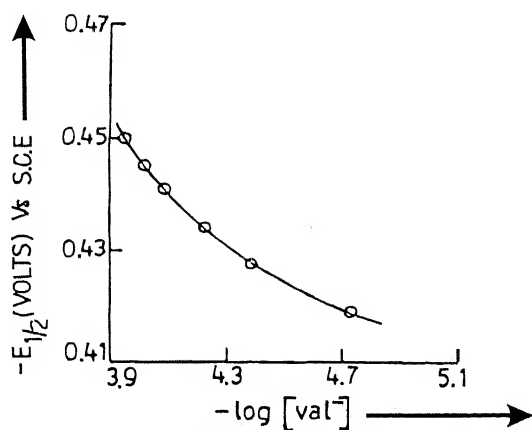


FIG. 4.15 PLOT OF $-E_{1/2}$ Vs $-\log [\text{val}^{2+}]$ FOR Pb (II) - DL - VALINE SYSTEM

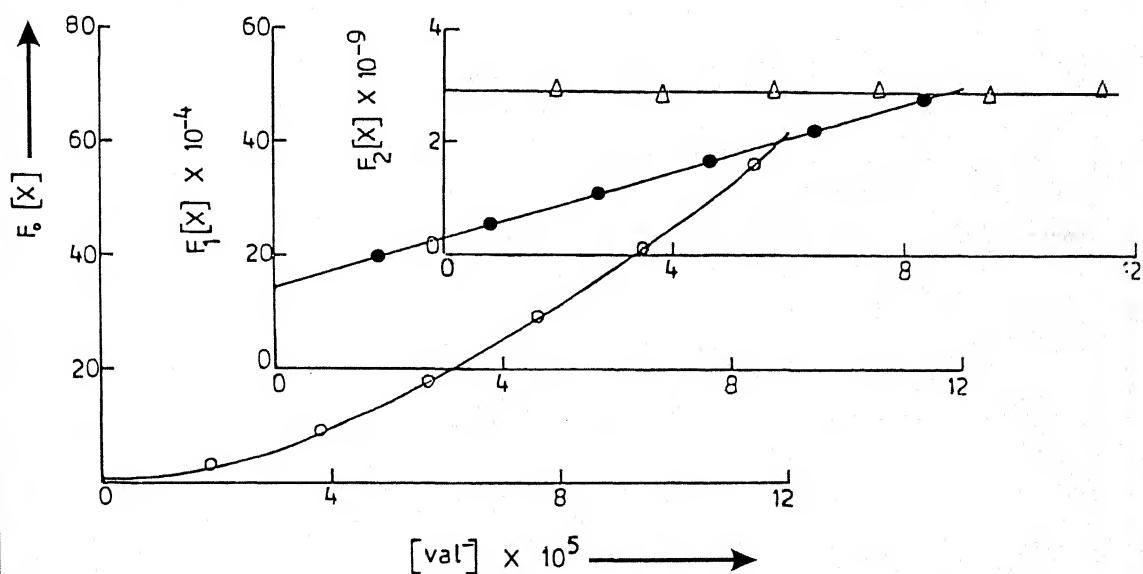


FIG. 4.16 PLOT OF $F_1 [X]$ Vs $[\text{val}^{2+}]$ FOR Pb (II) - DL - VALINE SYSTEM

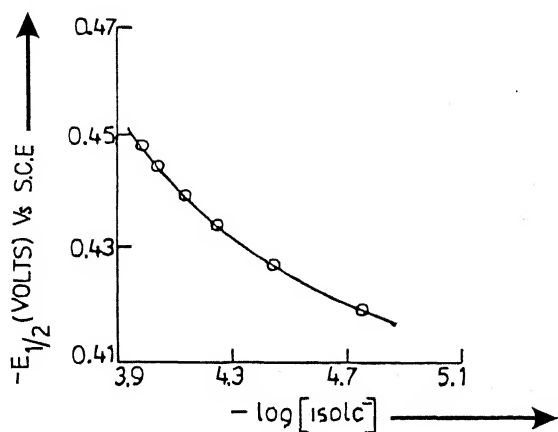


FIG. 4.17 PLOT OF $-E_{1/2}$ Vs $-\log [\text{isoleucine}]$ FOR Pb (II) - L - ISOLEUCINE SYSTEM

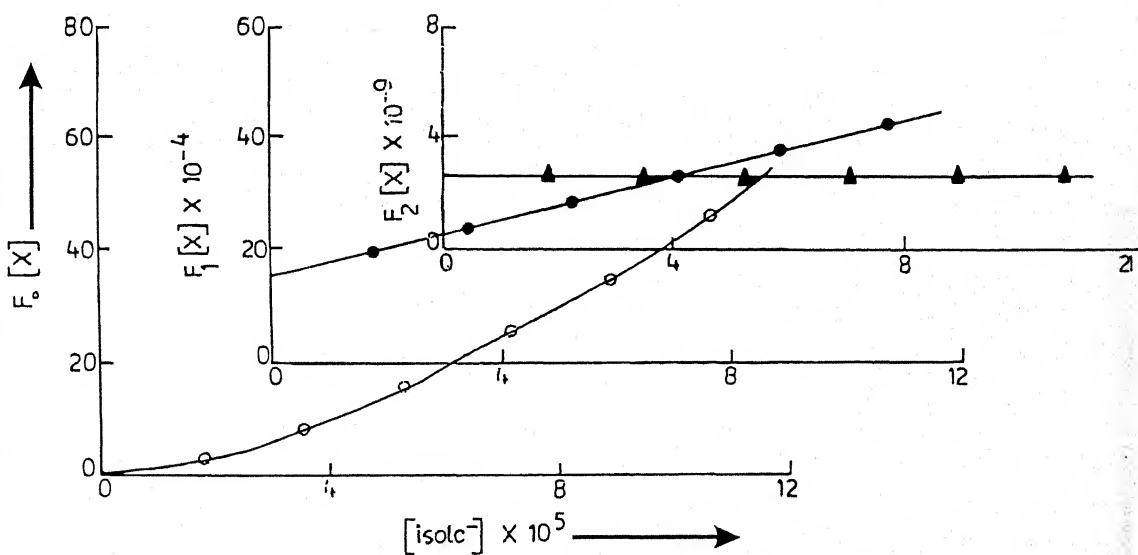


FIG. 4.18 PLOT OF $F [X]$ Vs $[\text{isoleucine}]$ FOR Pb (II) - L - ISOLEUCINE SYSTEM

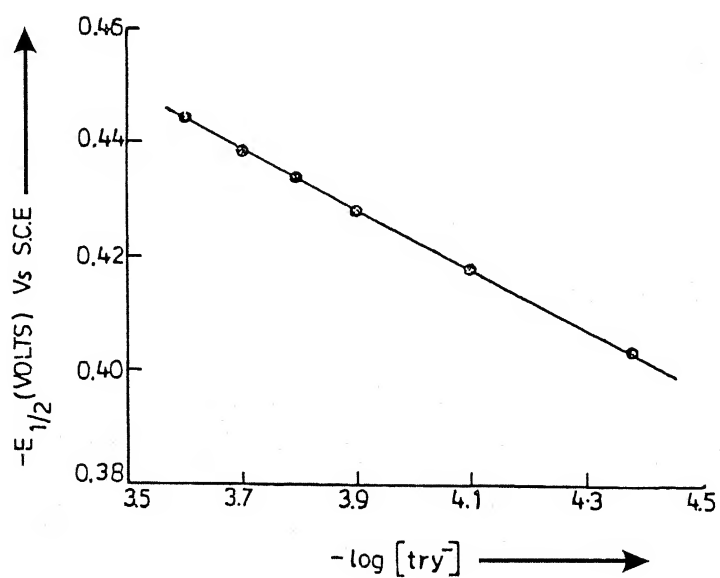


FIG. 4.19 PLOT OF $-E_{1/2}$ Vs $-\log [\text{try}^-]$ FOR Pb (II) - L - TRYPTOPHAN SYSTEM

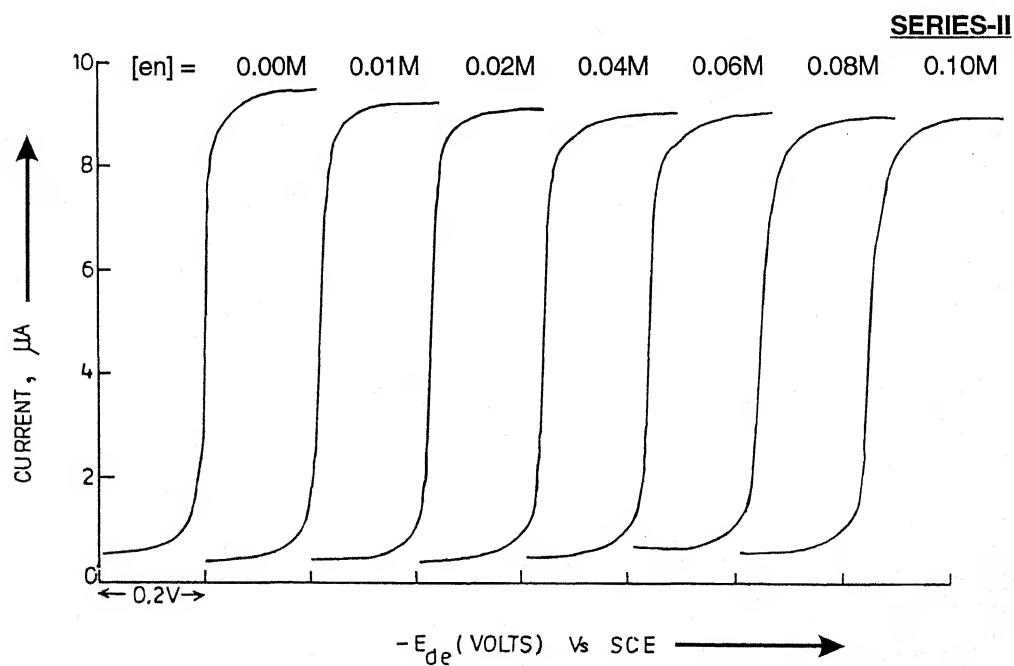
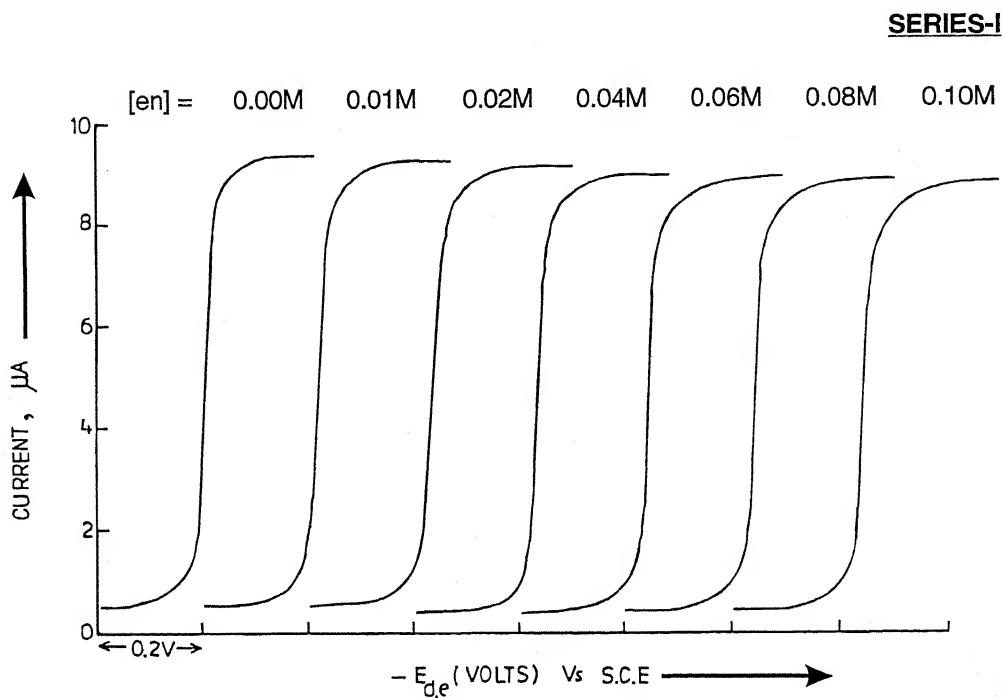
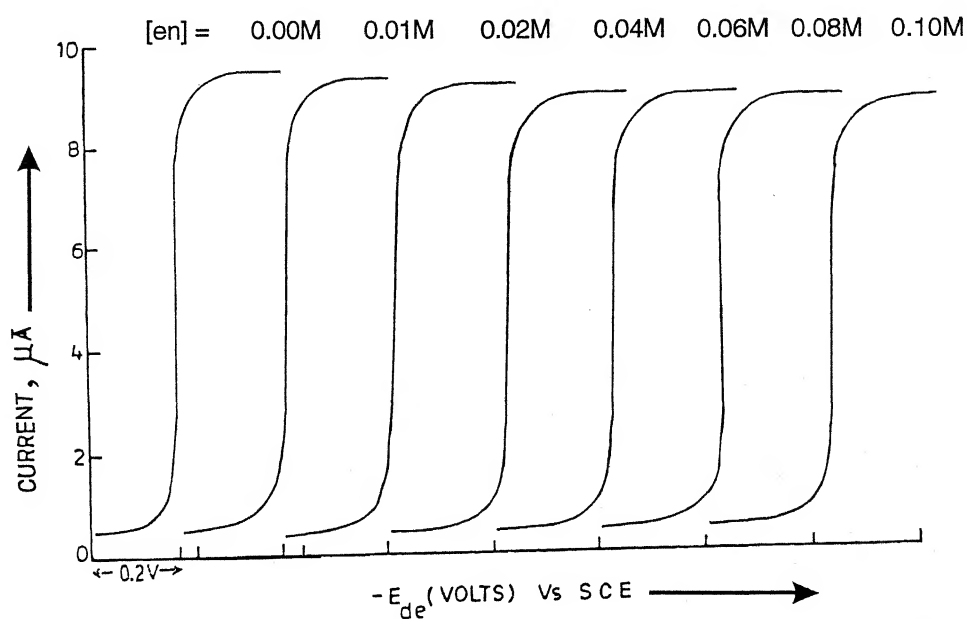


FIG. 4.20 POLAROGRAPHIC WAVES OF Pb(II) - ETHYLENEDIAMINE GLYCINE SYSTEM

SERIES-I



SERIES-II

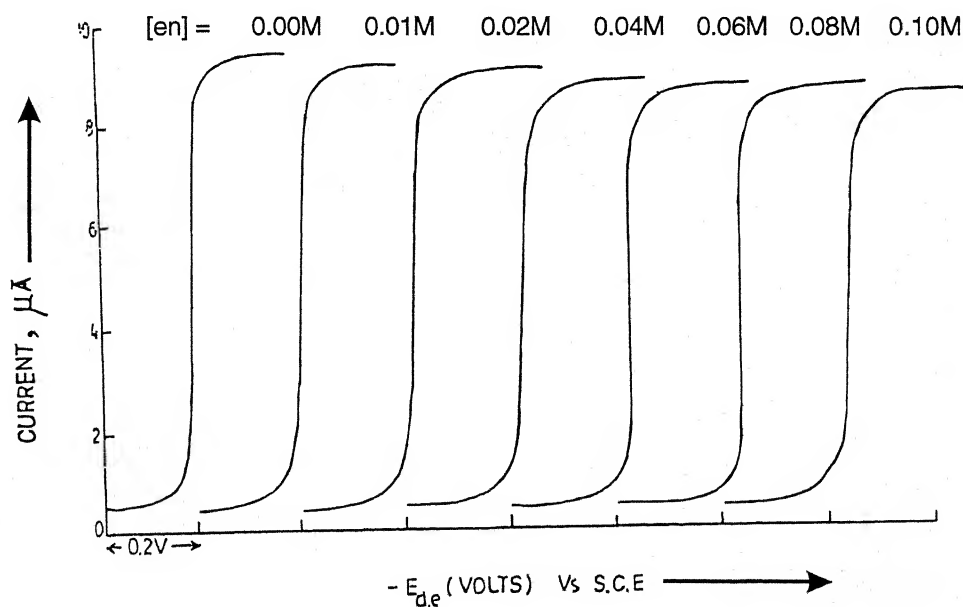


FIG. 4.21 POLAROGRAPHIC WAVES OF Pb (II) - ETHYLENEDIAMIN - DL - ALANINE SYSTEM

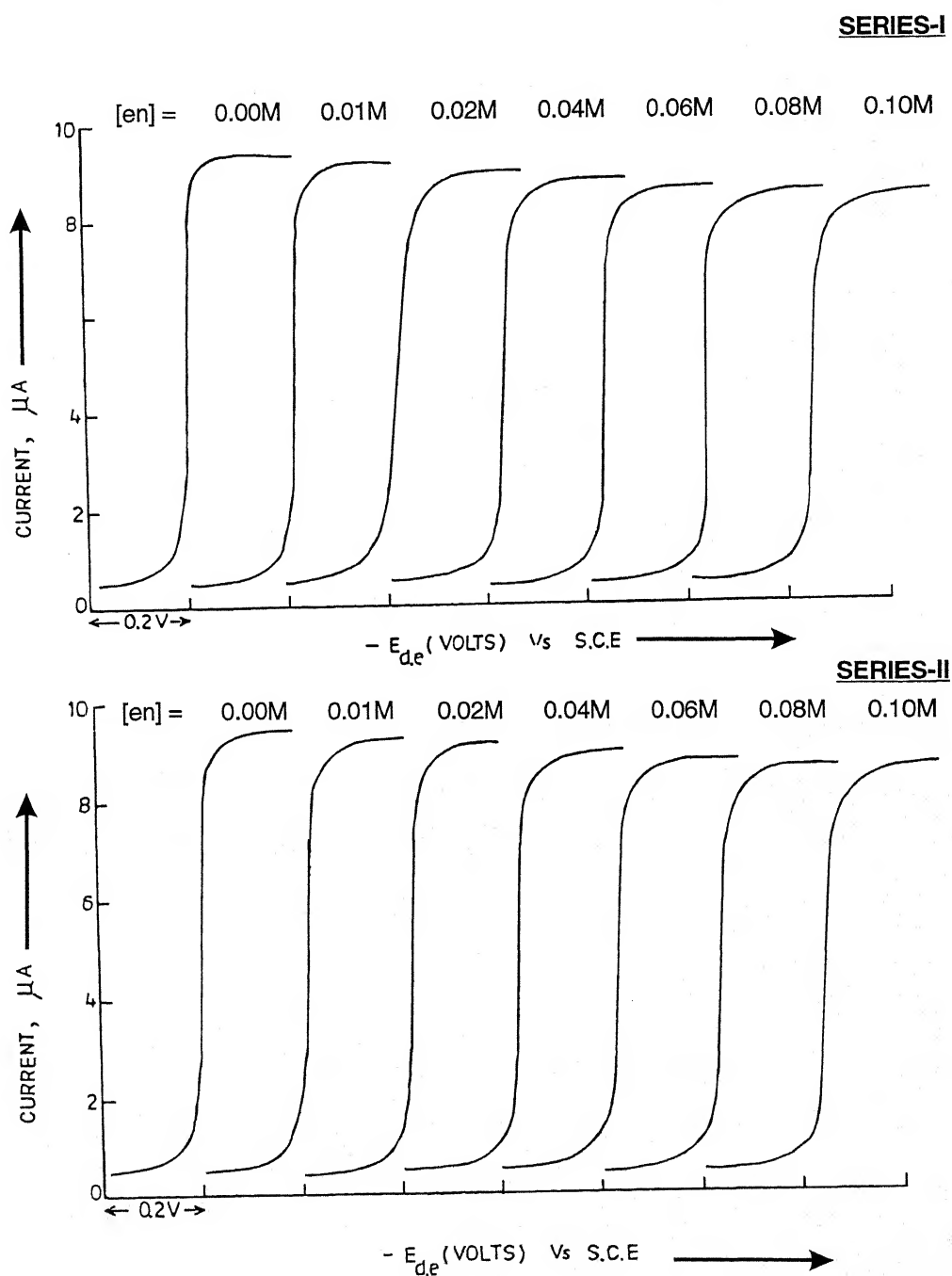


FIG. 4.22 POLAROGRAPHIC WAVES OF Pb (II) - ETHYLENEDIAMINE - DL - VALINE SYSTEM

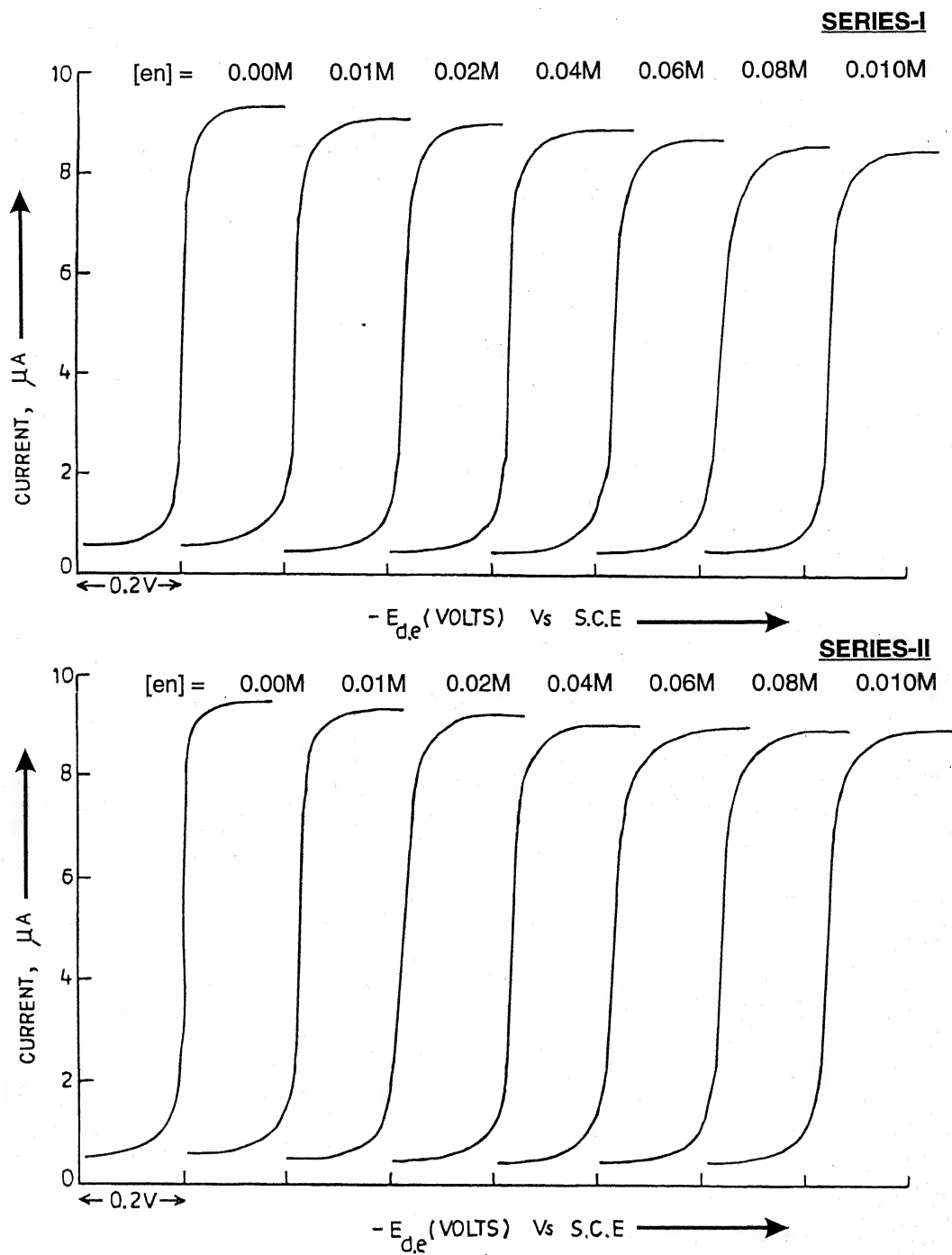


FIG. 4.23 POLAROGRAPHIC WAVES OF Pb (II) - ETHYLENEDIAMINE - L - ISOLEUCINE SYSTEM

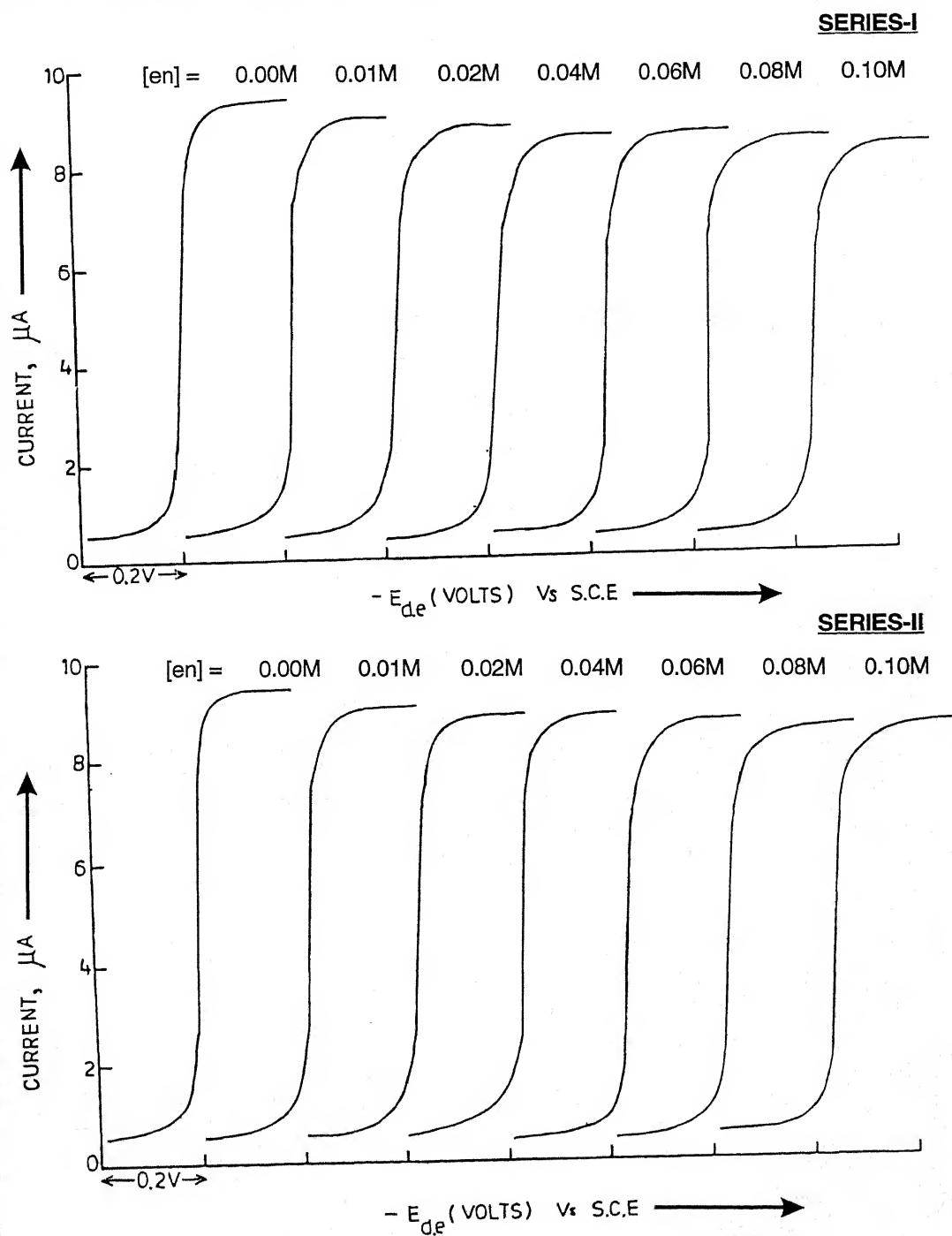


FIG. 4.24 POLAROGRAPHIC WAVES OF Pb (II) - ETHYLENEDIAMINE - L - TRYPTOPHAN SYSTEM

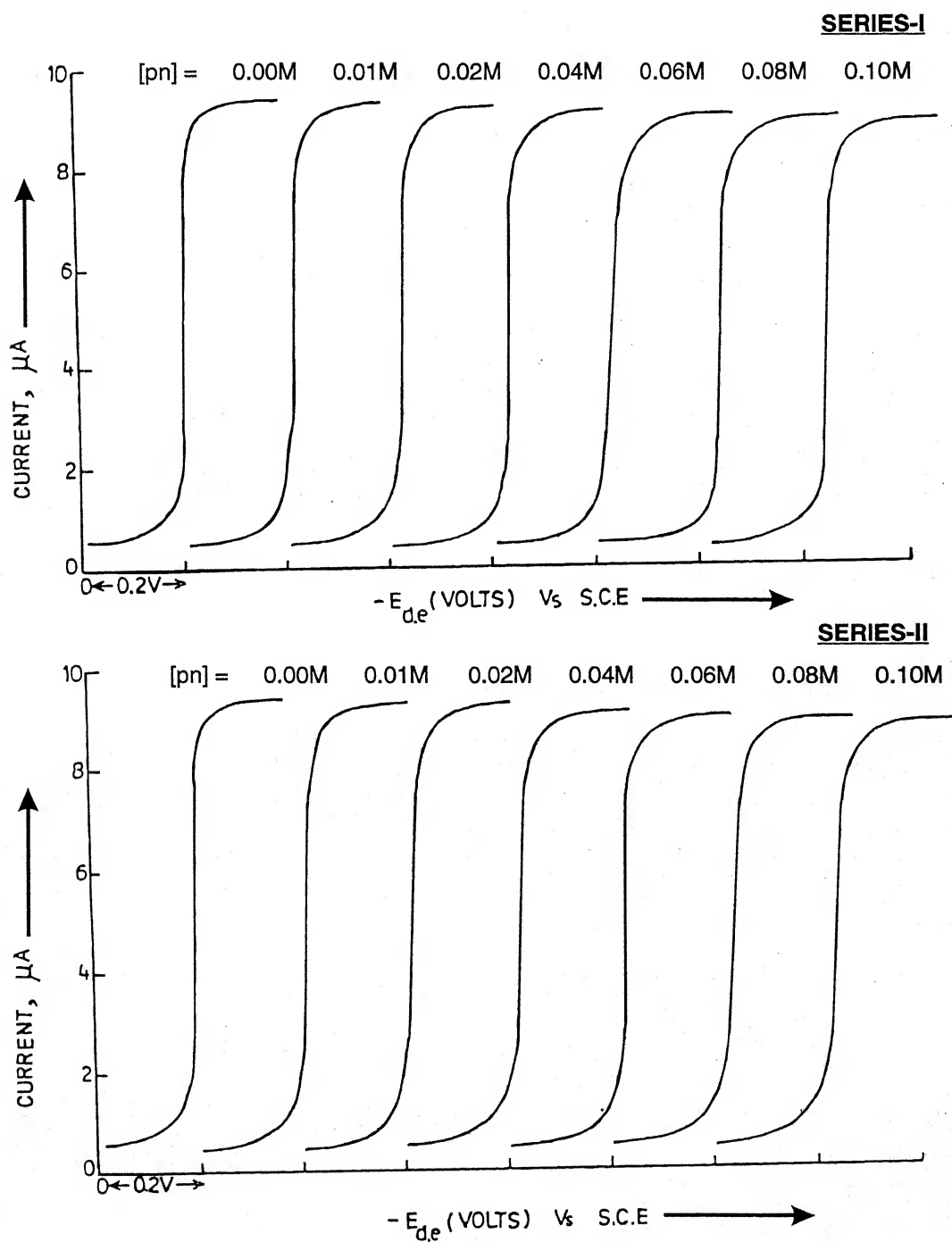


FIG. 4.25 POLAROGRAPHIC WAVES OF Pb (II) - PROPYLENEDIAMINE - GLYCINE SYSTEM

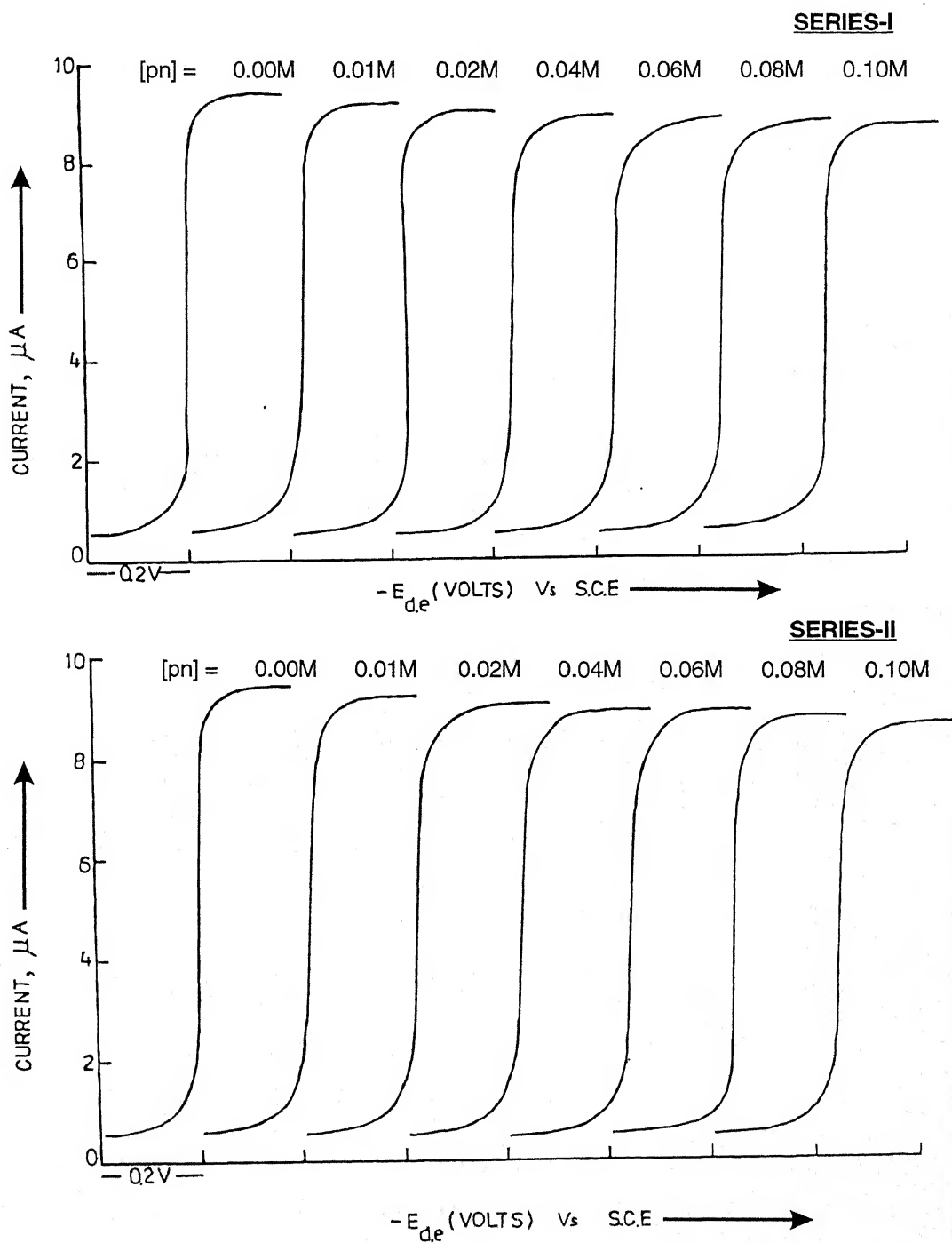


FIG. 4.26 POLAROGRAPHIC WAVES OF Pb (II) - PROYLENEDIAMINE - DL - ALANINE SYETEM

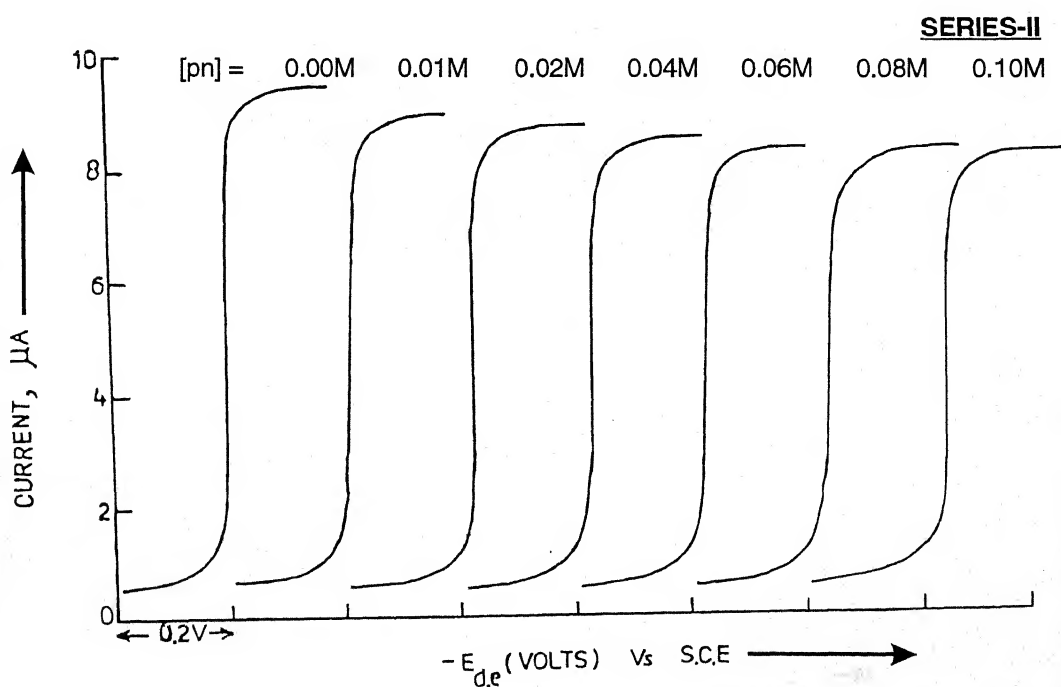
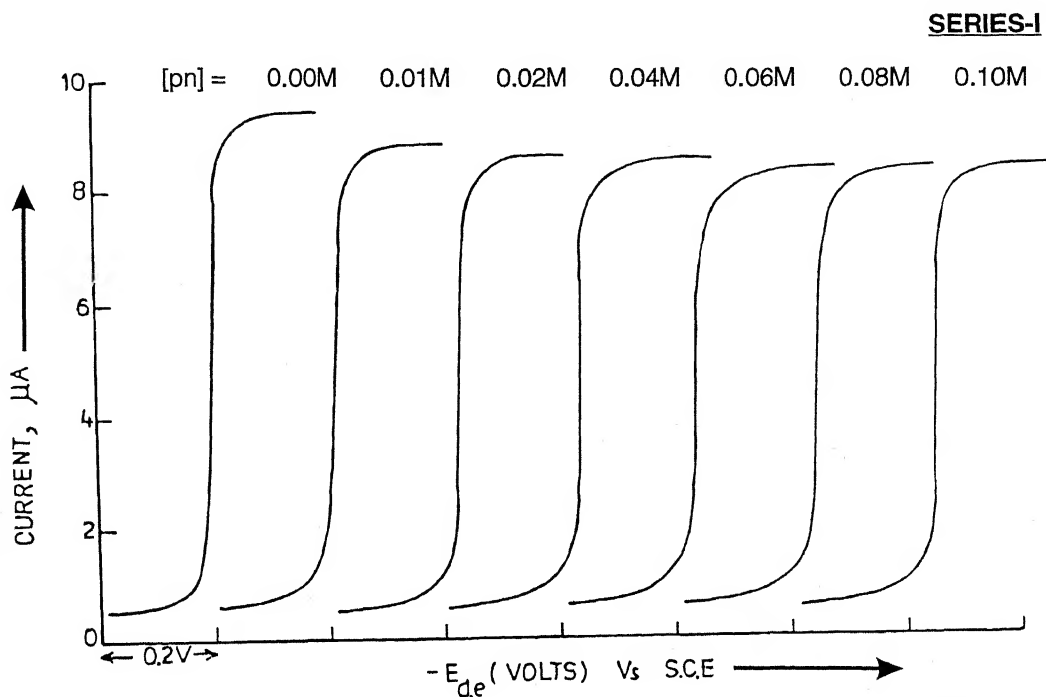


FIG. 4.27 POLAROGRAPHIC WAVES OF Pb (II) - PROPYLENEDIAMINE - DL - VALINE SYSTEM

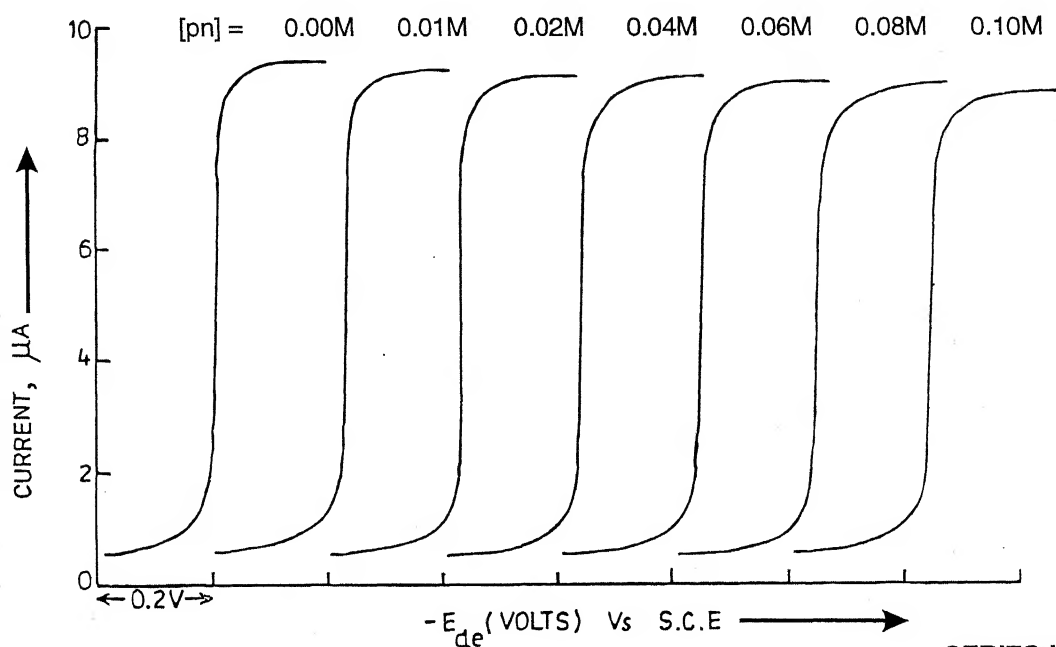
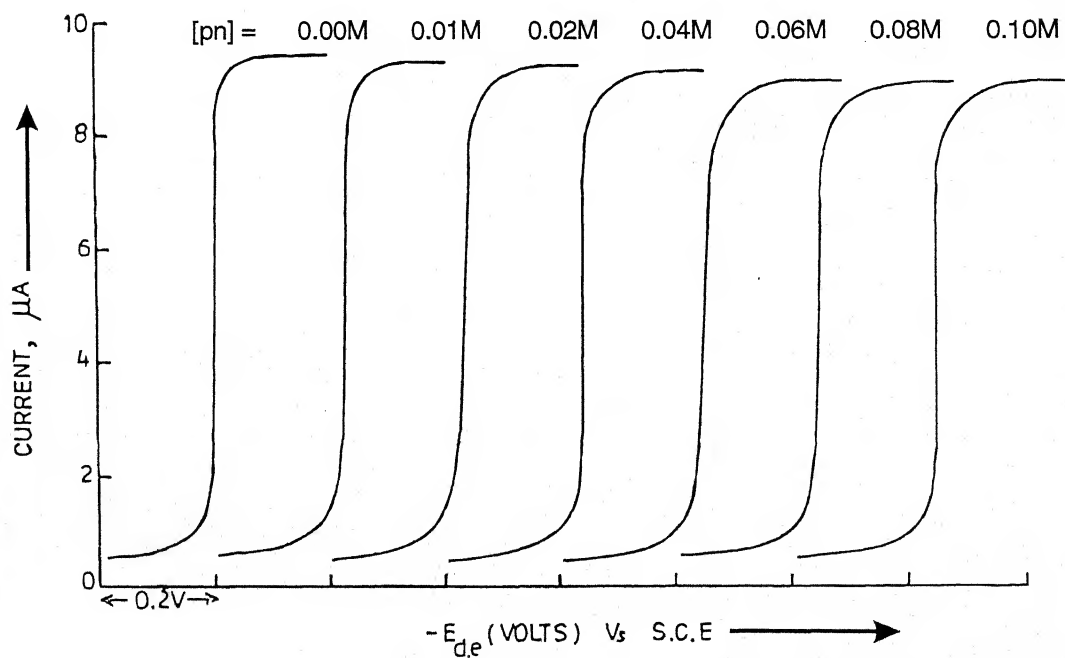
SERIES-I**SERIES-II**

FIG. 4.28 POLAROGRAPHIC WAVES OF Pb(II) - PROPYLENEDIAMINE - L - ISOLEUCINE SYSTEM

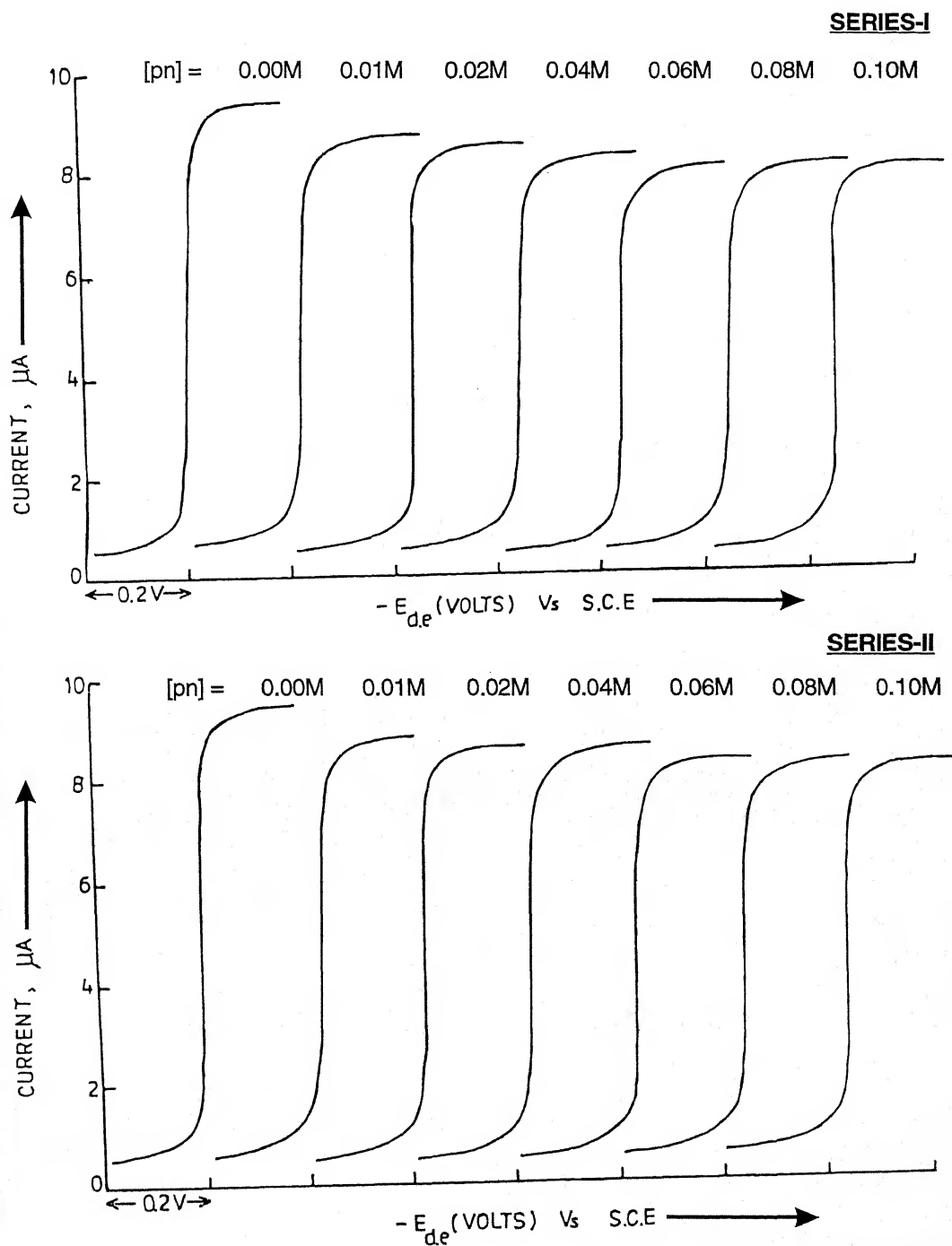
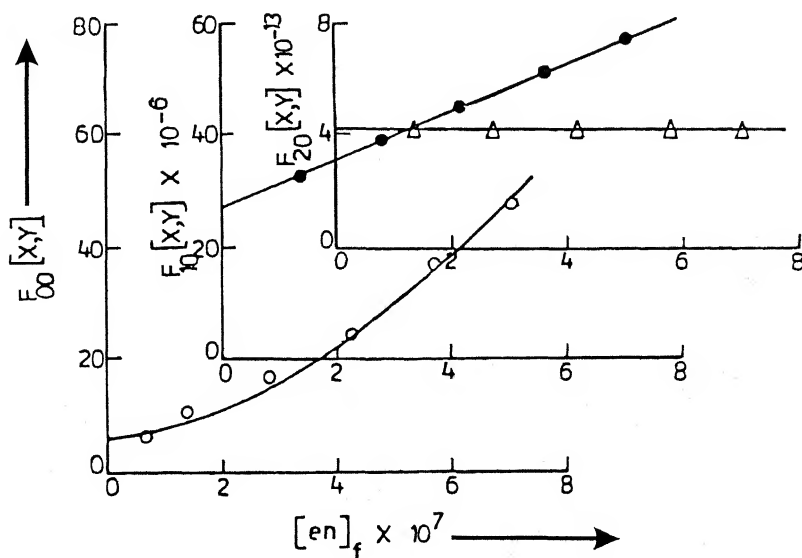


FIG. 4.29 POLAROGRAPHIC WAVES OF Pb (II) - PROPYLENEDIAMINE - L - TRYPTOPHAN SYSTEM

SERIES-I



SERIES-II

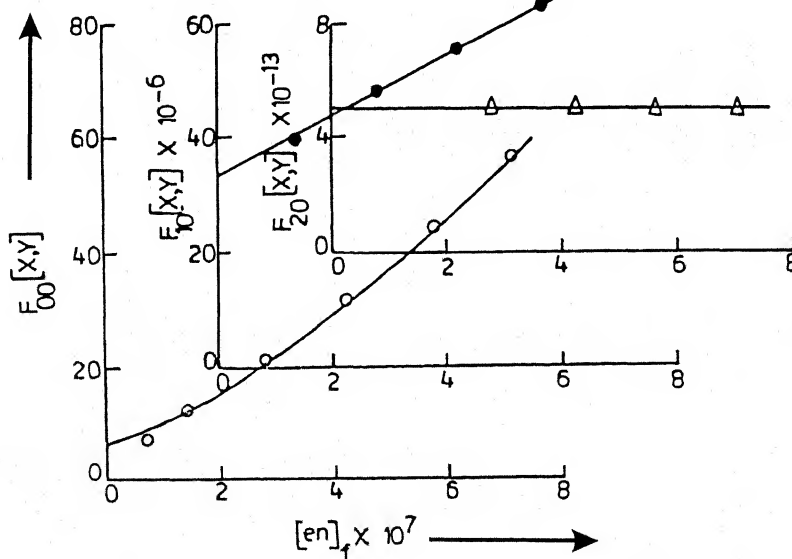
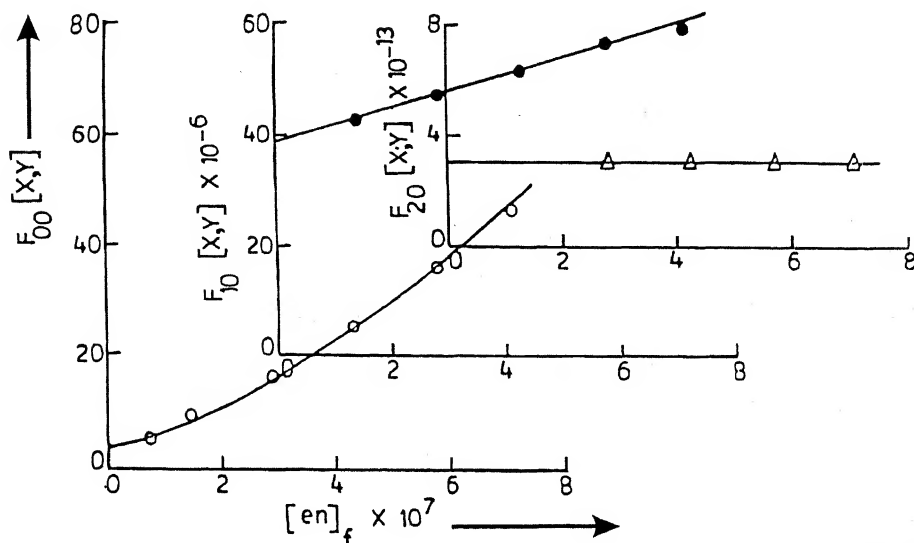


FIG. 4.30 PLOT OF $F_i[X,Y]$ FUNCTIONS FOR Pb(II) - ETHYLENEDIAMINE GLYCINE SYSTEM

SERIES-I



SERIES-II

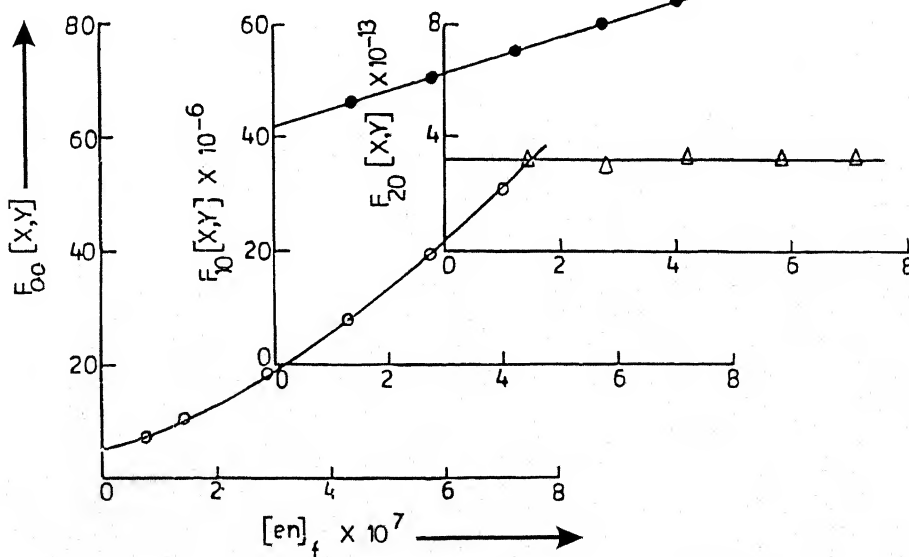
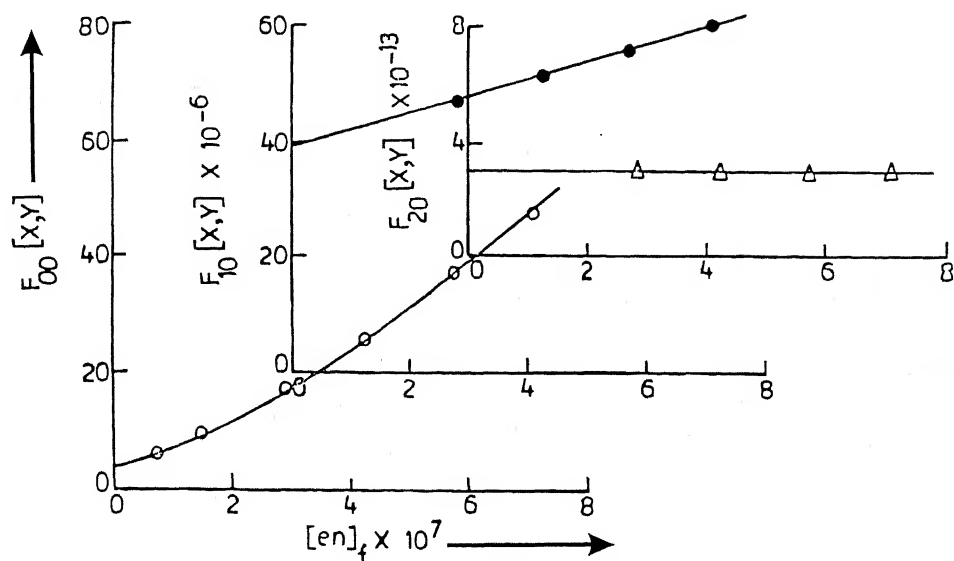


FIG. 4.31 PLOT OF $F_i[X,Y]$ FUNCTIONS FOR Pb (II) - ETHYLENEDIAMINE - DL - ALANINE SYSTEM

SERIES-I



SERIES-II

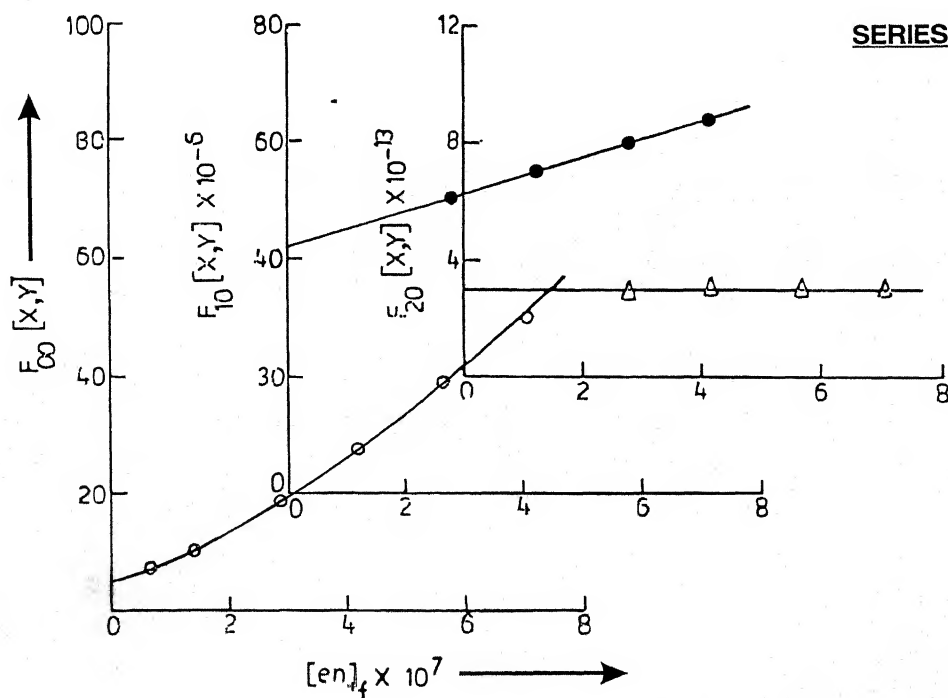
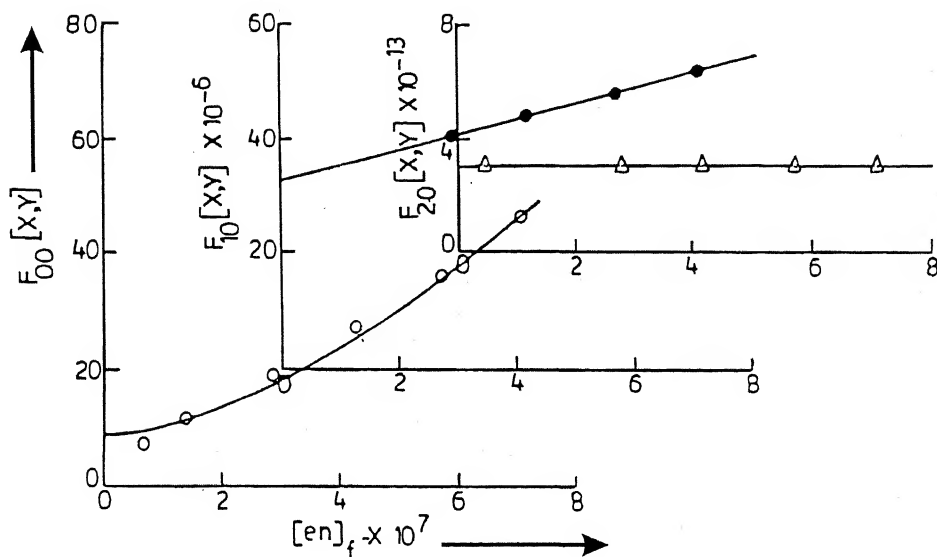


FIG. 4.32 PLOT OF $F_i[X,Y]$ FUNCTIONS FOR Pb (II) - ETHYLENEDIAMINE - DL - VALINE SYSTEM

SERIES-I



SERIES-II

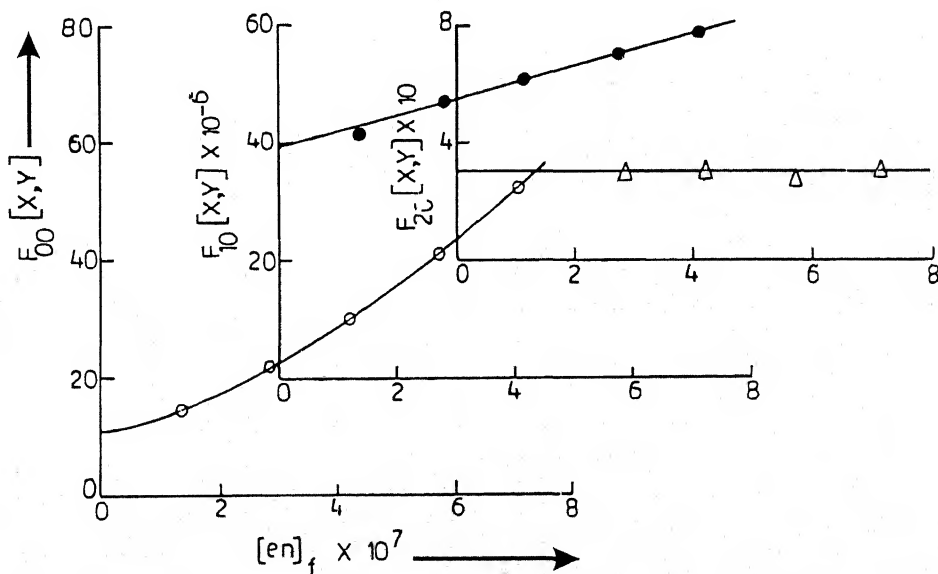
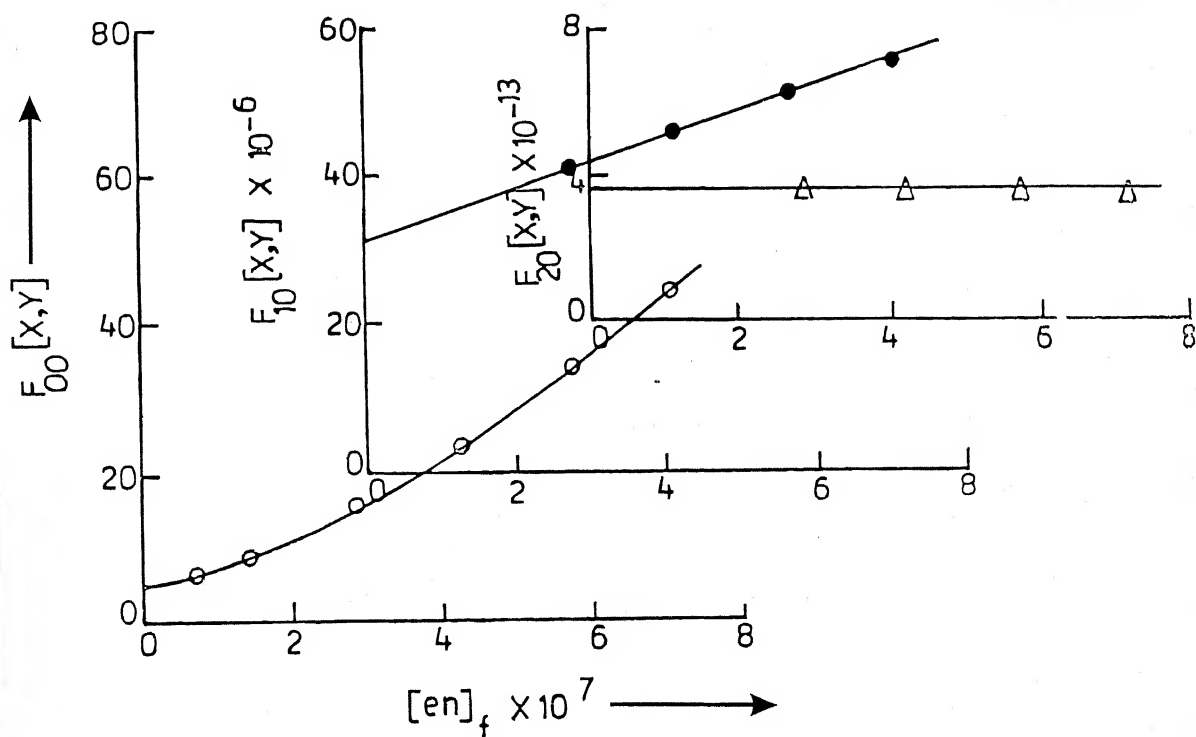


FIG. 4.33 PLOT OF $F_i[X,Y]$ FUNCTIONS FOR Pb (II) - ETHYLENEDIAMINE - L - ISOLEUCINE SYSTEM

SERIES-I



SERIES-II

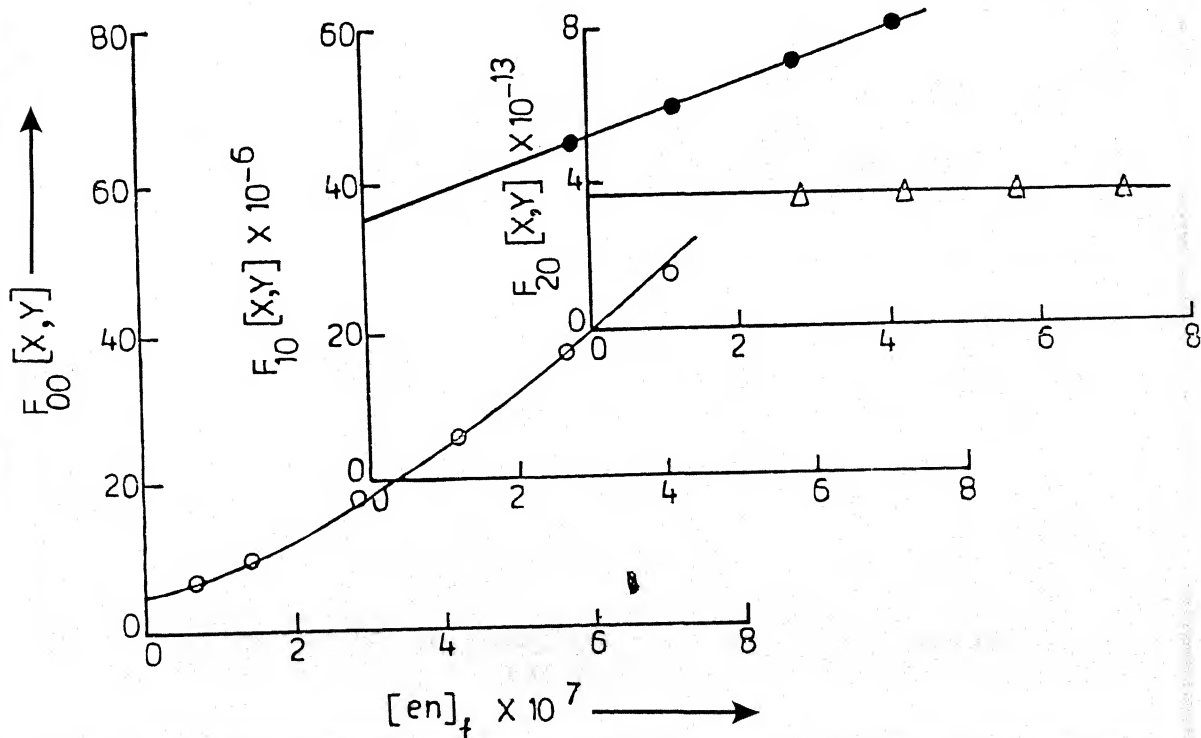
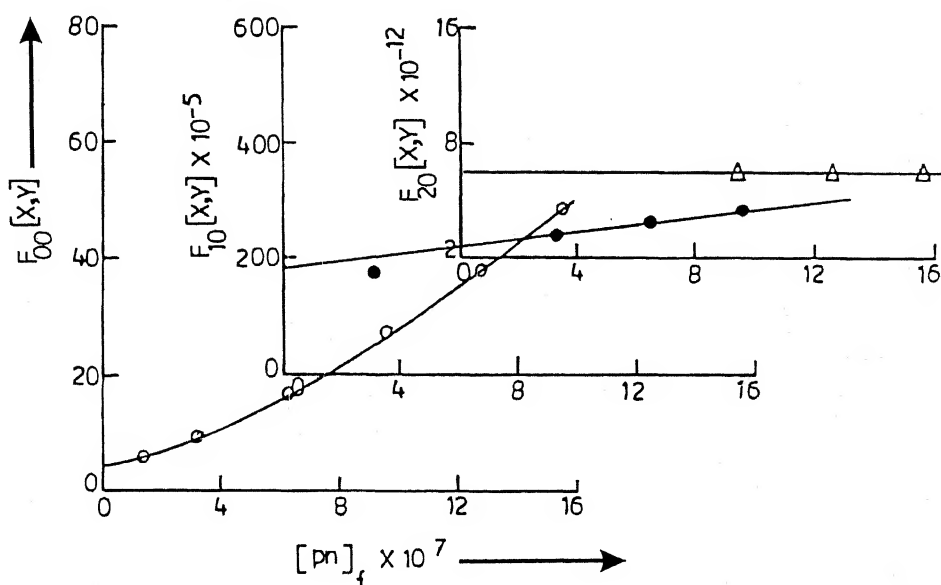


FIG. 4.34 PLOT OF $F_i[X,Y]$ FUNCTIONS FOR Pb(II) - ETHYLENEDIAMINE - L - TRYPTOPHAN SYSTEM

SERIES-I



SERIES-II

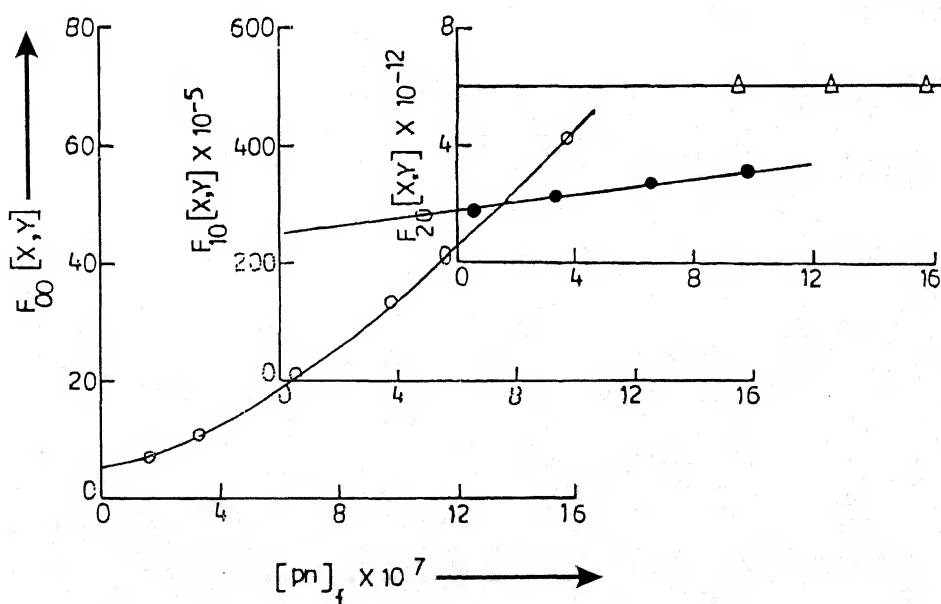


FIG. 4.35 PLOT OF $F_i[X,Y]$ FUNCTIONS FOR Pb (II) - PROPYLENEDIAMINE GLYCINE SYSTEM

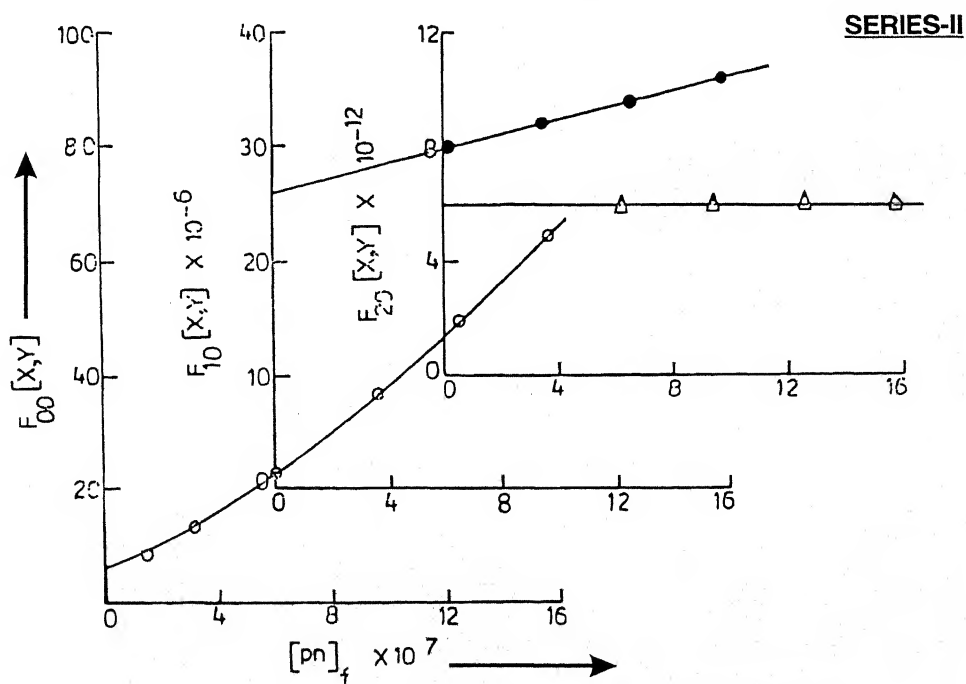
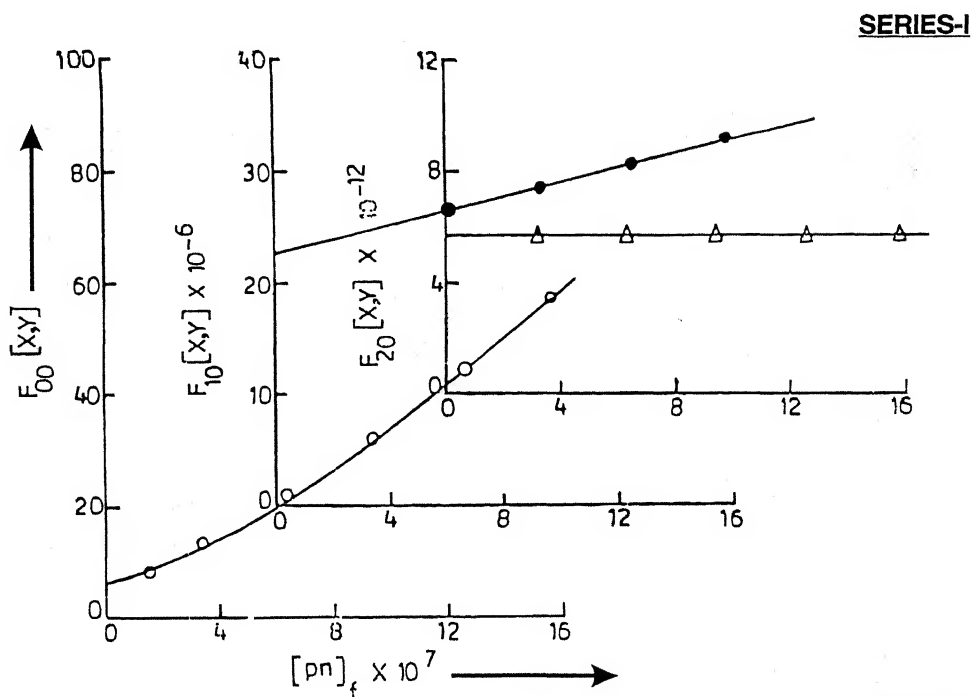


FIG. 4.36 PLOT OF $F_i [X,Y]$ FUNCTIONS FOR Pb (II) - PROPYLENEDIAMINE - DL - ALANINE SYSTEM

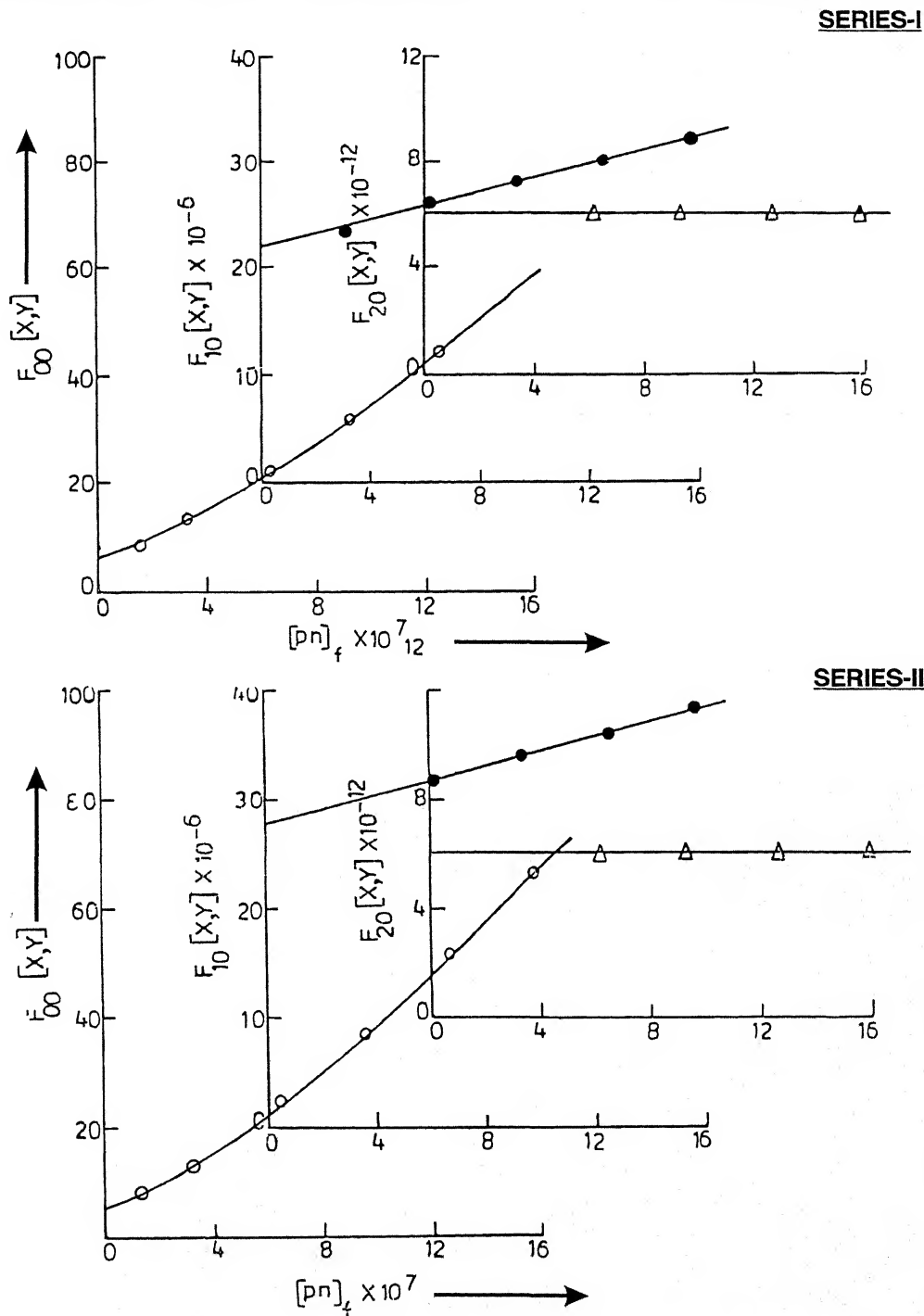


FIG. 4.37 PLOT OF $F_{ij}[X,Y]$ FUNCTIONS FOR Pb(II) - PROPYLENDIAMINE - DL - VALINE SYSTEM

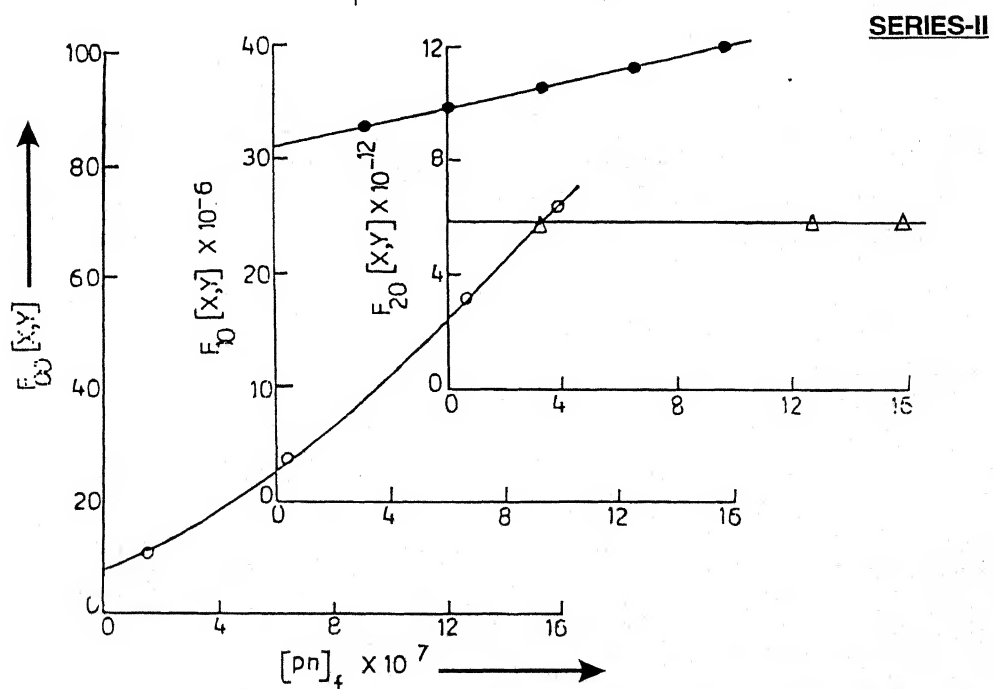
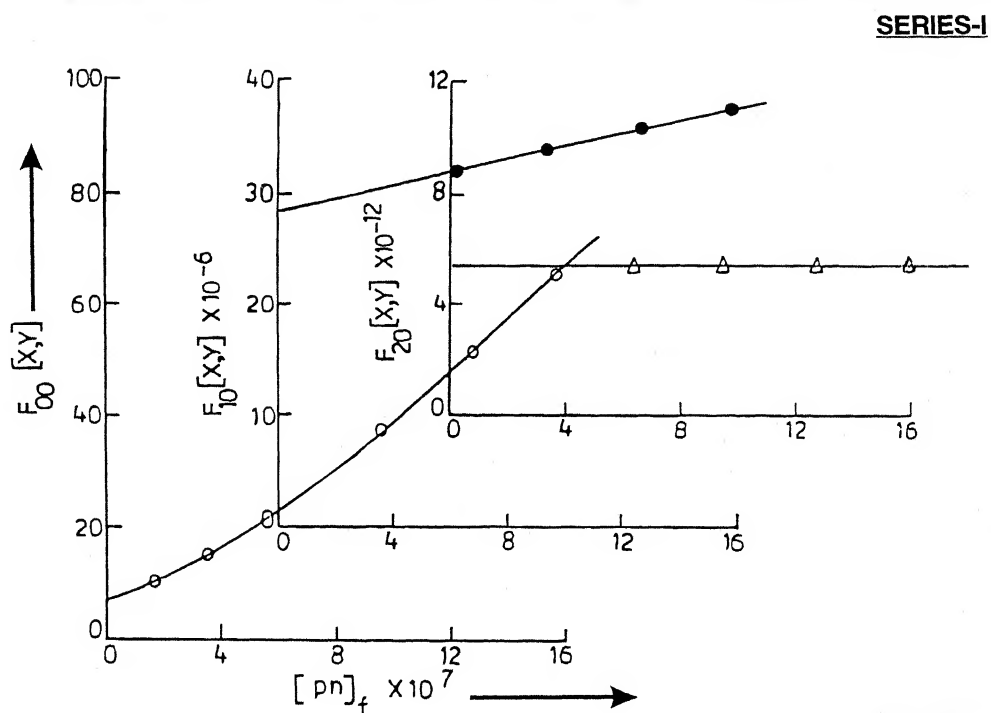
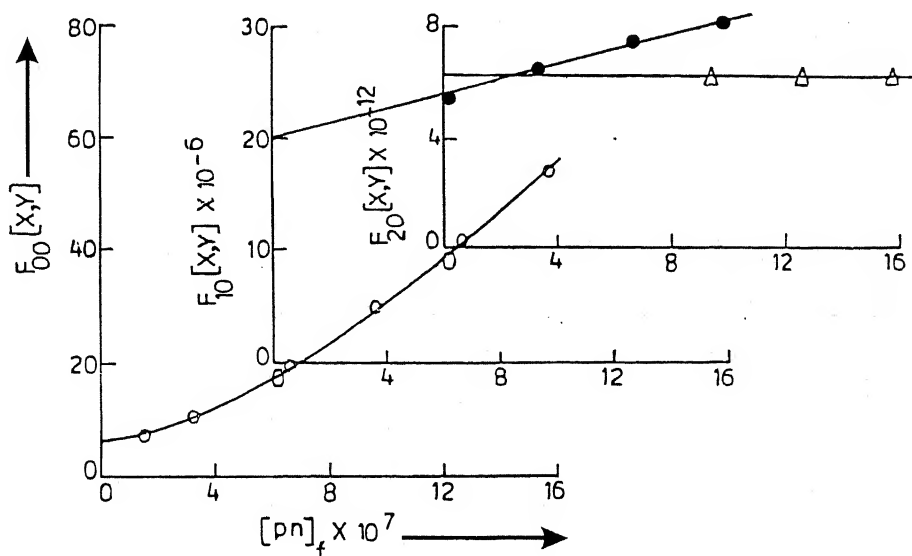


FIG. 4.38 PLOT OF $F_i[X,Y]$ FUNCTIONS FOR Pb (II) - PROPYLENEDIAMINE - L - ISOLEUCINE SYSTEM

SERIES-I



SERIES-II

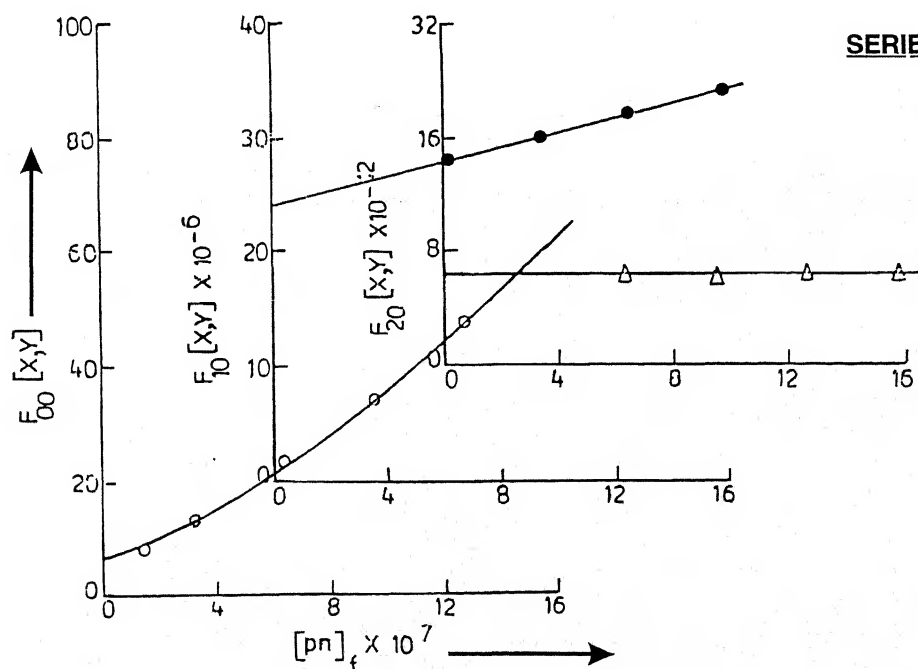


FIG. 4.39 PLOTS OF $F_i[X,Y]$ FUNCTIONS FOR Pb(II) - PROPYLENEDIAMINE - L - TRYPTOPHAN SYSTEM

TABLE 4.01

POLAROGRAPHIC FUNCTIONS OF THE SIMPLE Pb (II) - ETHYLENEDIAMINE SYSTEM

$[\text{en}]_t$ M	$[\text{en}]_f$ $\times 10^7$ M	$\log \frac{I_M}{I_C}$	$\Delta E_{1/2}$ V	Slope mV	$F_0 [x]$	$F_1 [x]$ $\times 10^{-6}$	$F_2 [x]$ $\times 10^{-13}$
0.00	0.0	—	—	29	—	—	—
0.01	0.7	0.143	0.008	29	1.93	13.12	—
0.02	1.4	0.178	0.019	30	4.58	25.39	3.11
0.04	2.8	0.0229	0.028	30	9.35	29.49	3.00
0.06	4.2	0.0239	0.034	31	14.95	32.91	2.80
0.08	5.7	0.0286	0.039	31	22.31	37.65	2.94
0.10	7.0	0.0327	0.043	31	30.77	42.11	3.00

$[\text{en}]_t$ = Total (analytical) concentration of ethylenediamine (en)

$[\text{en}]_f$ = Free ligand of ethylenediamine (en)

$[\text{Pb}^{2+}] = 1.0 \times 10^{-3} \text{ M}$, $\mu = 1.0$ (NaNO_3), $\text{pH} = 6.0$, $\text{Temp.} = 25 \pm 0.1^\circ\text{C}$

TABLE 4.02

POLAROGRAPHIC FUNCTIONS OF THE SIMPLE Pb (II) - PROPYLENEDIAMINE
SYSTEM

$[pn]_t$	$[pn]_f$	$\log \frac{I_M}{I_c}$	$\Delta E_{1/2}$	Slope	$F_0 [x]$	$F_1 [x]$	$F_2 [x]$
M	$\times 10^7$ M		V	mV		$\times 10^{-5}$	$\times 10^{-12}$
0.00	0.0	—	—	29	—	—	—
0.01	1.6	.0073	0.011	30	2.39	—	—
0.02	3.2	.0103	0.022	30	5.69	148.35	5.80
0.04	6.3	.0163	0.031	31	11.63	167.93	6.00
0.06	9.5	.0224	0.037	30	18.83	187.65	6.06
0.08	12.7	.0412	0.041	31	26.85	204.03	5.84
0.10	15.8	.0412	0.045	31	36.67	225.21	6.01

$[pn]_t$ = Total (analytical) concentration of propylenediamine (pn)

$[pn]_f$ = Free ligand of propylenediamine (pn)

$[Pb^{2+}] = 1.0 \times 10^{-3} \text{ M}$, $\mu = 1.0$ (NaNO₃), pH = 6.0, Temp. = $25 \pm 0.1^\circ\text{C}$

TABLE 4.03

POLAROGRAPHIC FUNCTIONS OF THE SIMPLE Pb (II) - GLYCINE SYSTEM

[gly]	[gly ⁻]	$\log \frac{I_M}{I_C}$	$\Delta E_{1/2}$	Slope	$F_0 [x]$	$F_1 [x]$	$F_2 [x]$
M	$\times 10^5$ M		V	mV		$\times 10^{-4}$	$\times 10^{-9}$
0.0	0.0	—	—	29	—	—	—
0.1	1.7	.0244	0.021	29	5.43	26.09	4.17
0.2	3.3	.0286	0.031	30	11.96	33.11	4.26
0.3	4.9	.0322	0.038	31	20.82	39.87	4.19
0.4	6.6	.0396	0.043	31	31.26	45.64	4.02
0.5	8.3	.0396	0.048	30	46.16	54.48	4.27
0.6	9.9	.0428	0.052	31	63.36	62.83	4.40

[gly] = Total (analytical) concentration of glycine (gly)

[gly⁻] = Glycinate ion concentration.

[Pb²⁺] = 1.0×10^{-3} M, $\mu = 1.0$ (NaNO₃), pH = 6.0, Temp. = $25 \pm 0.1^\circ\text{C}$

TABLE 4.04

POLAROGRAPHIC FUNCTIONS OF THE SIMPLE Pb (II) - DL - ALANINE SYSTEM

[ala] M	[ala ⁻] X 10 ⁵ M	log $\frac{I_M}{I_c}$	$\Delta E_{1/2}$ V	Slope mV
0.0	0.0	—	—	29
0.1	1.3	.0073	0.010	30
0.2	2.7	.0098	0.024	30
0.3	4.0	.0123	0.034	31
0.4	5.4	.0158	0.040	30
0.5	6.7	.0173	0.046	.31
0.6	8.1	.0178	0.049	31

[ala] = Total (analytical) concentration of alanine (ala)

[ala⁻] = Alanine ion concentration.

[Pb²⁺] = 1.0 X 10⁻³ M, μ = 1.0 (NaNO₃), pH = 6.0, Temp. = 25 ± 0.1°C

TABLE 4.05

POLAROGRAPHIC FUNCTIONS OF THE SIMPLE Pb (II) - DL - VALINE SYSTEM

[val]	[val ⁻]	$\log \frac{I_M}{I_C}$	$\Delta E_{1/2}$	Slope	F ₀ [x]	F ₁ [x]	F ₂ [x]
M	X 10 ⁵ M		V	mV		X 10 ⁻⁴	X 10 ⁻⁹
0.0	0.0	—	—	29	—	—	—
0.1	1.9	.0286	0.019	29	4.69	19.44	2.86
0.2	3.8	.0348	0.029	29	10.38	24.63	2.79
0.3	5.7	.0444	0.036	30	18.32	30.33	2.86
0.4	7.6	.0576	0.042	30	29.46	37.35	3.06
0.5	9.5	.0620	0.046	30	40.64	41.64	2.90
0.6	11.4	.0686	0.050	31	56.36	48.43	3.01

[val] = Total (analytical) concentration of valine (val)

[val⁻] = Valinate ion concentration.

[Pb²⁺] = 1.0 X 10⁻³ M, μ = 1.0 (NaNO₃), pH = 6.0, Temp. = 25 ± 0.1°C

TABLE 4.06

POLAROGRAPHIC FUNCTIONS OF THE SIMPLE Pb (II) - L - ISOLEUCINE SYSTEM

[isolc]	[isolc ⁻]	$\log \frac{I_M}{I_C}$	$\Delta E_{1/2}$	Slope	$F_0 [x]$	$F_1 [x]$	$F_2 [x]$
M	$\times 10^5$ M		V	mV		$\times 10^{-4}$	$\times 10^{-9}$
0.0	0.0	—	—	29	—	—	—
0.1	1.8	.0103	0.019	30	4.50	19.45	2.47
0.2	3.5	.0214	0.028	30	9.31	23.75	2.50
0.3	5.3	.0270	0.035	30	16.28	28.67	2.56
0.4	7.1	.0338	0.040	31	24.41	32.93	2.52
0.5	8.9	.0390	0.044	31	33.75	36.88	2.46
0.6	10.7	.0401	0.048	31	46.21	42.42	2.57

[isolc] = Total (analytical) concentration of isoleucine (isolc)

[isolc⁻] = Isoleucinate ion concentration.

[Pb²⁺] = 1.0×10^{-3} M, $\mu = 1.0$ (NaNO₃), pH = 6.0, Temp. = $25 \pm 0.1^\circ\text{C}$

TABLE 4.07

POLAROGRAPHIC FUNCTIONS OF THE SIMPLE Pb (II) - L - TRYPTOPHAN SYSTEM

[try] M	[try ⁻] X 10 ⁵ M	log $\frac{I_M}{I_c}$	$\Delta E_{1/2}$ V	Slope mV
0.0	0.0	—	—	29
0.1	4.1	0.0814	0.008	29
0.2	8.1	0.0885	0.018	30
0.3	12.2	0.0957	0.028	30
0.4	16.3	0.1014	0.034	30
0.5	20.4	0.1055	0.038	31
0.6	24.4	0.1061	0.044	31

[try] = Total (analytical) concentration of tryptophan (try)

[try⁻] = Tryptophan ion concentration.

[Pb²⁺] = 1.0 X 10⁻³ M, μ = 1.0 (NaNO₃), pH = 6.0, Temp. = 25 ± 0.1°C

TABLE 4.08

**POLAROGRAPHIC FUNCTIONS OF THE MIXED Pb (II) - ETHYLENEDIAMINE -
GLYCINE SYSTEM**

$[en]_t$	$[en]_f$	$\log \frac{I_M}{I_c}$	$\Delta E_{1/2}$	Slope	$F_{00} [X,Y]$	$F_{10} [X,Y]$	$F_{20} [X,Y]$
M	$\times 10^7$ M		V	mV		$\times 10^{-6}$	$\times 10^{-13}$
0.01	0.7	—	—	29	5.62	—	—
0.02	1.4	.0064	0.008	29	10.63	32.87	4.16
0.04	2.8	.0079	0.014	30	17.03	38.99	4.23
0.06	4.2	.0079	0.019	30	25.15	45.16	4.28
0.08	5.7	.0175	0.023	31	35.12	51.08	4.22
0.10	7.1	.0357	0.027	31	46.27	56.73	4.18

SERIES I : $[gly] = 0.2$ M

$[en]_t$	$[en]_f$	$\log \frac{I_M}{I_c}$	$\Delta E_{1/2}$	Slope	$F_{00} [X,Y]$	$F_{10} [X,Y]$	$F_{20} [X,Y]$
M	$\times 10^7$ M		V	mV		$\times 10^{-6}$	$\times 10^{-13}$
0.01	0.7	—	—	29	7.10	—	—
0.02	1.4	.0085	0.008	29	13.49	38.93	—
0.04	2.8	.0085	0.014	29	21.54	48.38	4.80
0.06	4.2	.0090	0.019	30	31.93	56.42	5.05
0.08	5.7	.0151	0.023	30	44.21	63.53	5.00
0.10	7.1	.0151	0.027	31	60.39	70.97	5.06

SERIES II : $[gly] = 0.3$ M

$[Pb^{2+}] = 1.0 \times 10^{-3}$ M, $\mu = 1.0$ (NaNO₃), pH = 6.0, Temp. = $25 \pm 0.1^\circ\text{C}$

TABLE 4.09

POLAROGRAPHIC FUNCTIONS OF THE MIXED Pb (II) - ETHYLENEDIAMINE**- DL - ALANINE SYSTEM**

$[en]_t$	$[en]_f$	$\log \frac{I_M}{I_c}$	$\Delta E_{1/2}$	Slope	$F_{00} [X,Y]$	$F_{10} [X,Y]$	$F_{20} [X,Y]$
M	$\times 10^7$ M		V	mV		$\times 10^{-6}$	$\times 10^{-13}$
0.01	0.7	—	—	29	4.86	—	—
0.02	1.4	.0105	0.009	29	10.02	42.69	2.62
0.04	2.8	.0167	0.016	30	17.53	47.83	3.11
0.06	4.2	.0198	0.021	30	26.14	52.22	3.11
0.08	5.7	.0245	0.025	31	36.09	56.70	3.11
0.10	7.1	.0400	0.028	31	47.26	60.93	3.09

SERIES I : $[ala] = 0.2 \text{ M}$

$[en]_t$	$[en]_f$	$\log \frac{I_M}{I_c}$	$\Delta E_{1/2}$	Slope	$F_{00} [X,Y]$	$F_{10} [X,Y]$	$F_{20} [X,Y]$
M	$\times 10^7$ M		V	mV		$\times 10^{-6}$	$\times 10^{-13}$
0.01	0.7	—	—	29	7.17	—	—
0.02	1.4	.0050	0.006	29	11.55	46.45	3.15
0.04	2.8	.0239	0.012	30	19.30	50.54	3.02
0.06	4.2	.0239	0.017	30	28.48	55.38	3.15
0.08	5.7	.0250	0.021	30	39.02	60.11	3.19
0.10	7.1	.0351	0.024	31	50.45	64.28	3.15

SERIES II : $[ala] = 0.3 \text{ M}$

$[Pb^{2+}] = 1.0 \times 10^{-3} \text{ M}$, $\mu = 1.0$ ($NaNO_3$), pH = 6.0, Temp. = $25 \pm 0.1^\circ C$

TABLE 4.10

POLAROGRAPHIC FUNCTIONS OF THE MIXED Pb (II) - ETHYLENEDIAMINE**- DL - VALINE SYSTEM**

$[en]_t$	$[en]_f$	$\log \frac{I_M}{I_c}$	$\Delta E_{1/2}$	Slope	$F_{00} [X,Y]$	$F_{10} [X,Y]$	$F_{20} [X,Y]$
M	$\times 10^7$ M		V	mV		$\times 10^{-6}$	$\times 10^{-13}$
0.01	0.7	—	—	29	6.17	—	—
0.02	1.4	.0096	0.006	29	10.07	39.48	—
0.04	2.8	.0230	0.013	30	17.90	47.36	2.95
0.06	4.2	.0241	0.018	30	26.52	51.93	3.04
0.08	5.7	.0288	0.022	31	36.62	56.75	3.13
0.10	7.1	.0358	0.025	31	47.02	60.14	3.00

SERIES I : [val] = 0.2 M

$[en]_t$	$[en]_f$	$\log \frac{I_M}{I_c}$	$\Delta E_{1/2}$	Slope	$F_{00} [X,Y]$	$F_{10} [X,Y]$	$F_{20} [X,Y]$
M	$\times 10^7$ M		V	mV		$\times 10^{-6}$	$\times 10^{-13}$
0.01	0.7	—	—	29	7.23	—	—
0.02	1.4	.0050	0.004	30	9.99	—	—
0.04	2.8	.0189	0.012	30	19.25	50.38	2.96
0.06	4.2	.0189	0.017	31	28.43	55.26	3.12
0.08	5.7	.0189	0.021	31	38.83	59.78	3.14
0.10	7.1	.0289	0.024	31	50.20	63.94	3.10

SERIES II : [val] = 0.3 M

$[Pb^{2+}] = 1.0 \times 10^{-3} \text{ M}$, $\mu = 1.0$ (NaNO₃), pH = 6.0, Temp. = $25 \pm 0.1^\circ\text{C}$

TABLE 4.11

POLAROGRAPHIC FUNCTIONS OF THE MIXED Pb (II) - ETHYLENEDIAMINE**- L - ISOLEUCINE SYSTEM**

$[en]_t$	$[en]_f$	$\log \frac{I_M}{I_c}$	$\Delta E_{1/2}$	Slope	$F_{00} [X,Y]$	$F_{10} [X,Y]$	$F_{20} [X,Y]$
M	$\times 10^7$ M		V	mV		$\times 10^{-6}$	$\times 10^{-13}$
0.01	0.7	—	—	29	7.27	—	—
0.02	1.4	.0040	0.007	29	12.66	25.96	—
0.04	2.8	.0071	0.013	30	20.35	40.11	2.86
0.06	4.2	.0071	0.017	30	27.79	44.33	2.91
0.08	5.7	.0232	0.020	31	36.44	48.49	2.91
0.10	7.1	.0259	0.023	31	46.32	52.79	2.94

SERIES I : [Isolc] = 0.2 M

$[en]_t$	$[en]_f$	$\log \frac{I_M}{I_c}$	$\Delta E_{1/2}$	Slope	$F_{00} [X,Y]$	$F_{10} [X,Y]$	$F_{20} [X,Y]$
M	$\times 10^7$ M		V	mV		$\times 10^{-6}$	$\times 10^{-13}$
0.01	0.7	—	—	29	8.36	—	—
0.02	1.4	.0040	0.008	29	15.74	40.70	—
0.04	2.8	.0075	0.013	29	23.43	47.44	2.98
0.06	4.2	.0080	0.017	30	32.02	51.96	3.05
0.08	5.7	.0218	0.020	31	41.78	56.15	3.03
0.10	7.1	.0218	0.023	31	53.10	60.71	3.05

SERIES II : [Isolc] = 0.3 M $[Pb^{2+}] = 1.0 \times 10^{-3} \text{ M}$, $\mu = 1.0$ (NaNO₃), pH = 6.0, Temp. = $25 \pm 0.1^\circ\text{C}$

TABLE 4.12

POLAROGRAPHIC FUNCTIONS OF THE MIXED Pb (II) - ETHYLENEDIAMINE- L - TRYPTOPHAN SYSTEM

$[en]_t$	$[en]_f$	$\log \frac{I_M}{I_C}$	$\Delta E_{1/2}$	Slope	$F_{00} [X,Y]$	$F_{10} [X,Y]$	$F_{20} [X,Y]$
M	$\times 10^7$ M		V	mV		$\times 10^{-6}$	$\times 10^{-13}$
0.01	0.7	—	—	29	6.89	—	—
0.02	1.4	.0062	0.005	29	9.56	32.34	—
0.04	2.8	.0099	0.011	30	16.64	41.12	3.57
0.06	4.2	.0110	0.016	30	24.61	46.25	3.59
0.08	5.7	.0157	0.020	31	34.00	51.24	3.57
0.10	7.1	.0477	0.023	31	45.19	56.61	3.60

SERIES I : $[try] = 0.2 \text{ M}$

$[en]_t$	$[en]_f$	$\log \frac{I_M}{I_C}$	$\Delta E_{1/2}$	Slope	$F_{00} [X,Y]$	$F_{10} [X,Y]$	$F_{20} [X,Y]$
M	$\times 10^7$ M		V	mV		$\times 10^{-6}$	$\times 10^{-13}$
0.01	0.7	—	—	29	7.34	—	—
0.02	1.4	.0103	0.006	29	10.26	37.34	—
0.04	2.8	.0114	0.011	30	17.77	45.11	3.57
0.06	4.2	.0129	0.016	30	26.24	50.31	3.61
0.08	5.7	.0192	0.020	31	36.40	55.48	3.62
0.10	7.1	.0388	0.023	31	48.23	60.88	3.64

SERIES II : $[try] = 0.3 \text{ M}$ $[Pb^{2+}] = 1.0 \times 10^{-3} \text{ M}$, $\mu = 1.0$ ($NaNO_3$), $pH = 6.0$, $Temp. = 25 \pm 0.1^\circ C$

TABLE 4.13

POLAROGRAPHIC FUNCTIONS OF THE MIXED Pb (II) - PROPYLENEDIAMINEGLYCINE SYSTEM

$[pn]_t$	$[pn]_f$	$\log \frac{I_M}{I_c}$	$\Delta E_{1/2}$	Slope	$F_{00} [X,Y]$	$F_{10} [X,Y]$	$F_{20} [X,Y]$
M	$\times 10^7$ M		V	mV		$\times 10^{-5}$	$\times 10^{-12}$
0.01	1.6	—	—	29	6.07	—	—
0.02	3.2	.0044	0.007	29	10.58	176.77	—
0.04	6.3	.0144	0.014	30	18.69	216.34	5.74
0.06	9.5	.0144	0.019	30	27.59	237.89	6.09
0.08	12.7	.0175	0.023	30	37.74	258.44	6.19
0.10	15.8	.0237	0.026	31	48.64	275.54	6.03

SERIES I : $[gly] = 0.2 \text{ M}$

$[pn]_t$	$[pn]_f$	$\log \frac{I_M}{I_c}$	$\Delta E_{1/2}$	Slope	$F_{00} [X,Y]$	$F_{10} [X,Y]$	$F_{20} [X,Y]$
M	$\times 10^7$ M		V	mV		$\times 10^{-5}$	$\times 10^{-12}$
0.01	1.6	—	—	29	7.13	—	—
0.02	3.2	.0025	0.006	29	11.44	172.28	—
0.04	6.3	.0100	0.015	30	23.48	276.15	—
0.06	9.5	.0120	0.020	30	34.83	308.77	6.19
0.08	12.7	.0130	0.024	30	47.69	329.02	6.23
0.10	15.8	.0207	0.027	31	61.32	349.22	6.26

SERIES II : $[gly] = 0.3 \text{ M}$ $[Pb^{2+}] = 1.0 \times 10^{-3} \text{ M}$, $\mu = 1.0$ ($NaNO_3$), $pH = 6.0$, $Temp. = 25 \pm 0.1^\circ C$

TABLE 4.14

POLAROGRAPHIC FUNCTIONS OF THE MIXED Pb (II) - PROPYLENEDIAMINE**- DL - ALANINE SYSTEM**

$[pn]_t$	$[pn]_f$	$\log \frac{I_M}{I_C}$	$\Delta E_{1/2}$	Slope	$F_{00} [X,Y]$	$F_{10} [X,Y]$	$F_{20} [X,Y]$
M	$\times 10^7$ M		V	mV		$\times 10^{-6}$	$\times 10^{-12}$
0.01	1.6	—	—	29	7.88	—	—
0.02	3.2	.0046	0.008	29	14.85	24.85	5.79
0.04	6.3	.0097	0.014	29	23.89	26.69	5.84
0.06	9.5	.0128	0.018	30	33.07	28.49	5.78
0.08	12.7	.0175	0.022	30	45.54	30.42	5.85
0.10	15.8	.0217	0.025	31	58.11	32.65	5.84

SERIES I : [ala] = 0.2 M

$[pn]_t$	$[pn]_f$	$\log \frac{I_M}{I_C}$	$\Delta E_{1/2}$	Slope	$F_{00} [X,Y]$	$F_{10} [X,Y]$	$F_{20} [X,Y]$
M	$\times 10^7$ M		V	mV		$\times 10^{-6}$	$\times 10^{-12}$
0.01	1.6	—	—	29	6.74	—	—
0.02	3.2	.0035	0.007	29	12.67	19.54	—
0.04	6.3	.0097	0.016	30	25.92	29.89	6.14
0.06	9.5	.0097	0.021	30	38.28	31.75	6.18
0.08	12.7	.0227	0.024	31	49.83	33.81	6.16
0.10	15.8	.0276	0.027	31	63.66	35.77	6.16

SERIES II : [ala] = 0.3 M $[Pb^{2+}] = 1.0 \times 10^{-3} \text{ M}$, $\mu = 1.0 \text{ (NaNO}_3\text{)}$, pH = 6.0, Temp. = $25 \pm 0.1^\circ\text{C}$

TABLE 4.15

POLAROGRAPHIC FUNCTIONS OF THE MIXED Pb (II) - PROPYLENEDIAMINE**- DL - VALINE SYSTEM**

$[pn]_t$	$[pn]_f$	$\log \frac{I_M}{I_c}$	$\Delta E_{1/2}$	Slope	$F_{00} [X,Y]$	$F_{10} [X,Y]$	$F_{20} [X,Y]$
M	$\times 10^7$ M		V	mV		$\times 10^{-6}$	$\times 10^{-12}$
0.01	1.6	—	—	29	7.65	—	—
0.02	3.2	.0042	0.008	29	14.41	23.45	—
0.04	6.3	.0096	0.014	30	23.29	25.73	5.89
0.06	9.5	.0117	0.018	30	34.47	27.66	5.95
0.08	12.7	.0200	0.022	31	44.49	29.59	5.99
0.10	15.8	.0244	0.025	31	56.79	31.43	5.95

SERIES I : [val] = 0.2 M

$[pn]_t$	$[pn]_f$	$\log \frac{I_M}{I_c}$	$\Delta E_{1/2}$	Slope	$F_{00} [X,Y]$	$F_{10} [X,Y]$	$F_{20} [X,Y]$
M	$\times 10^7$ M		V	mV		$\times 10^{-6}$	$\times 10^{-12}$
0.01	1.6	—	—	29	7.54	—	—
0.02	3.2	.0063	0.009	29	15.42	26.66	—
0.04	6.3	.0148	0.016	29	27.15	31.83	6.05
0.06	9.5	.0148	0.020	30	40.09	33.67	6.00
0.08	12.7	.0285	0.024	30	52.14	35.63	6.01
0.10	15.8	.0313	0.027	31	66.46	37.54	6.02

SERIES II : [val] = 0.3 M $[Pb^{2+}] = 1.0 \times 10^{-3} \text{ M}$, $\mu = 1.0$ (NaNO₃), pH = 6.0, Temp. = $25 \pm 0.1^\circ\text{C}$

TABLE 4.16

POLAROGRAPHIC FUNCTIONS OF THE MIXED Pb (II) - PROPYLENEDIAMINE**- L - ISOLEUCINE SYSTEM**

$[pn]_t$	$[pn]_f$	$\log \frac{I_M}{I_c}$	$\Delta E_{1/2}$	Slope	$F_{00} [X,Y]$	$F_{10} [X,Y]$	$F_{20} [X,Y]$
M	$\times 10^7$ M		V	mV		$\times 10^{-6}$	$\times 10^{-12}$
0.01	1.6	—	—	29	10.63	—	—
0.02	3.2	.0045	0.005	30	15.87	28.06	—
0.04	6.3	.0070	0.012	30	27.54	32.44	5.44
0.06	9.5	.0111	0.017	31	41.04	34.15	5.42
0.08	12.7	.0162	0.020	31	52.47	35.89	5.43
0.10	15.8	.0162	0.023	31	66.29	37.43	5.40

SERIES I : [Isolc] = 0.2 M

$[pn]_t$	$[pn]_f$	$\log \frac{I_M}{I_c}$	$\Delta E_{1/2}$	Slope	$F_{00} [X,Y]$	$F_{10} [X,Y]$	$F_{20} [X,Y]$
M	$\times 10^7$ M		V	mV		$\times 10^{-6}$	$\times 10^{-12}$
0.01	1.6	—	—	29	10.57	—	—
0.02	3.2	.0030	0.007	29	18.37	32.82	5.80
0.04	6.3	.0121	0.013	30	29.94	34.67	5.80
0.06	9.5	.0177	0.018	30	44.79	36.67	5.81
0.08	12.7	.0177	0.021	31	56.59	38.35	5.80
0.10	15.8	.0198	0.024	31	71.82	40.29	5.86

SERIES II : [Isolc] = 0.3 M $[Pb^{2+}] = 1.0 \times 10^{-3} \text{ M}$, $\mu = 1.0$ (NaNO₃), pH = 6.0, Temp. = $25 \pm 0.1^\circ\text{C}$

TABLE 4.17

POLAROGRAPHIC FUNCTIONS OF THE MIXED Pb (II) - PROPYLENEDIAMINE- L - TRYPTOPHAN SYSTEM

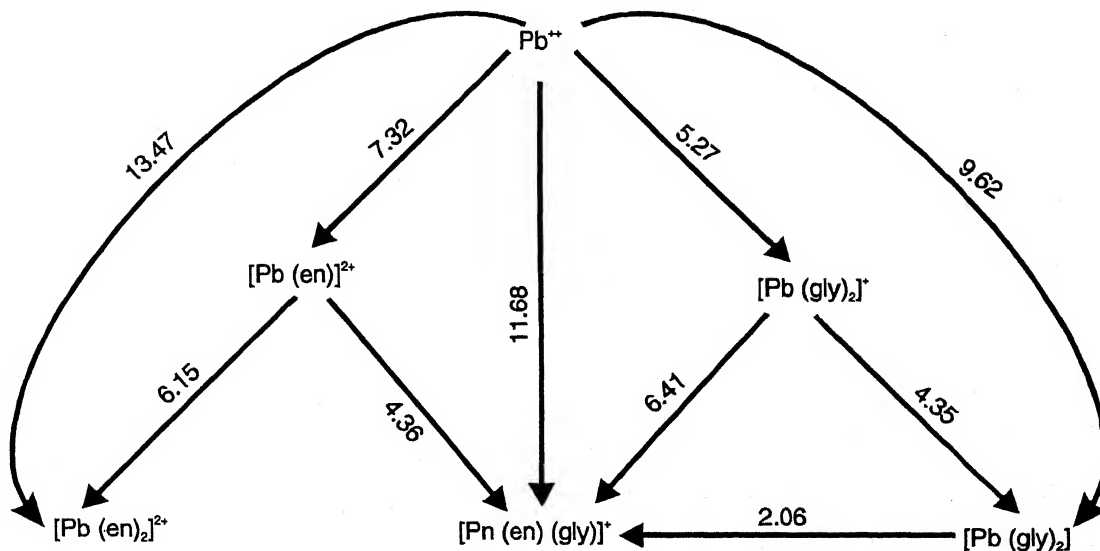
$[pn]_t$	$[pn]_f$	$\log \frac{I_M}{I_c}$	$\Delta E_{1/2}$	Slope	$F_{00} [X,Y]$	$F_{10} [X,Y]$	$F_{20} [X,Y]$
M	$\times 10^7$ M		V	mV		$\times 10^{-6}$	$\times 10^{-12}$
0.01	1.6	—	—	29	7.15	—	—
0.02	3.2	.0049	0.006	29	11.55	—	—
0.04	6.3	.0192	0.013	30	20.58	23.04	—
0.06	9.5	.0231	0.018	30	30.68	25.98	6.30
0.08	12.7	.0231	0.022	30	41.91	28.03	6.33
0.10	15.8	.0276	0.025	31	53.49	29.99	6.30

SERIES I : [try] = 0.2 M

$[pn]_t$	$[pn]_f$	$\log \frac{I_M}{I_c}$	$\Delta E_{1/2}$	Slope	$F_{00} [X,Y]$	$F_{10} [X,Y]$	$F_{20} [X,Y]$
M	$\times 10^7$ M		V	mV		$\times 10^{-6}$	$\times 10^{-12}$
0.01	1.6	—	—	29	8.26	—	—
0.02	3.2	.0037	0.007	29	14.37	23.33	—
0.04	6.3	.0048	0.014	29	24.85	28.21	6.64
0.06	9.5	.0048	0.019	30	36.72	30.33	6.66
0.08	12.7	.0200	0.012	30	48.04	32.39	6.62
0.10	15.8	.0267	0.025	31	61.49	34.49	6.63

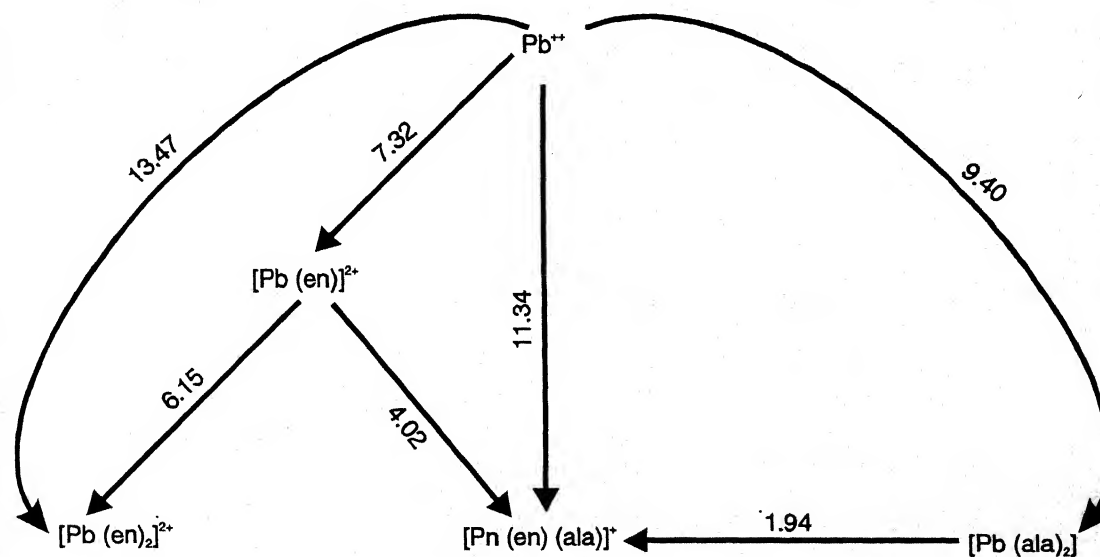
SERIES II : [try] = 0.3 M

[Pb²⁺] = 1.0 $\times 10^{-3}$ M, μ = 1.0 (NaNO₃), pH = 6.0, Temp. = 25 \pm 0.1°C



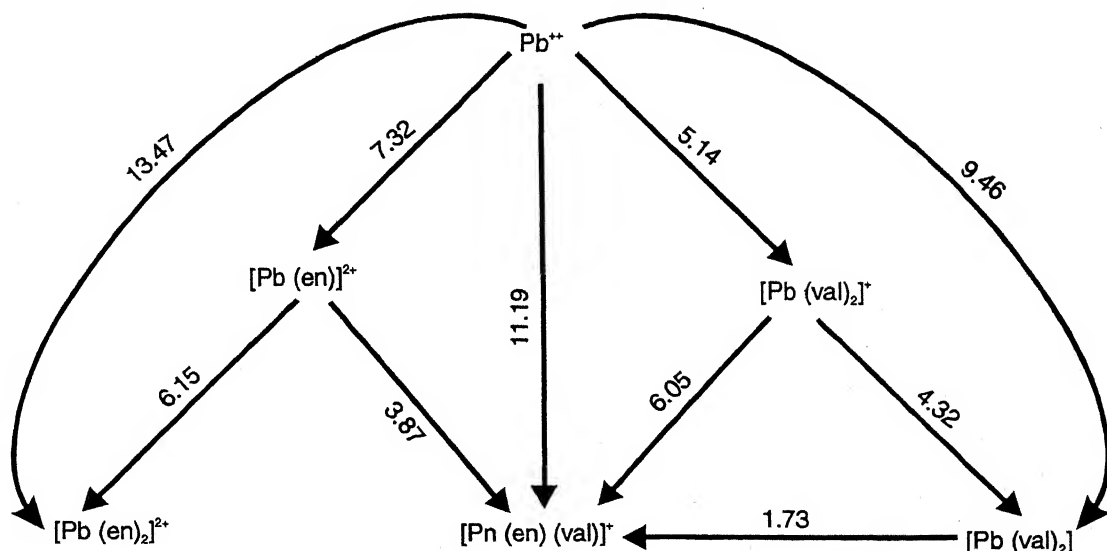
FLWSHEET DIAGRAM - 4.01

LEAD - ETHYLENEDIAMINE - GYLICINE SYSTEM



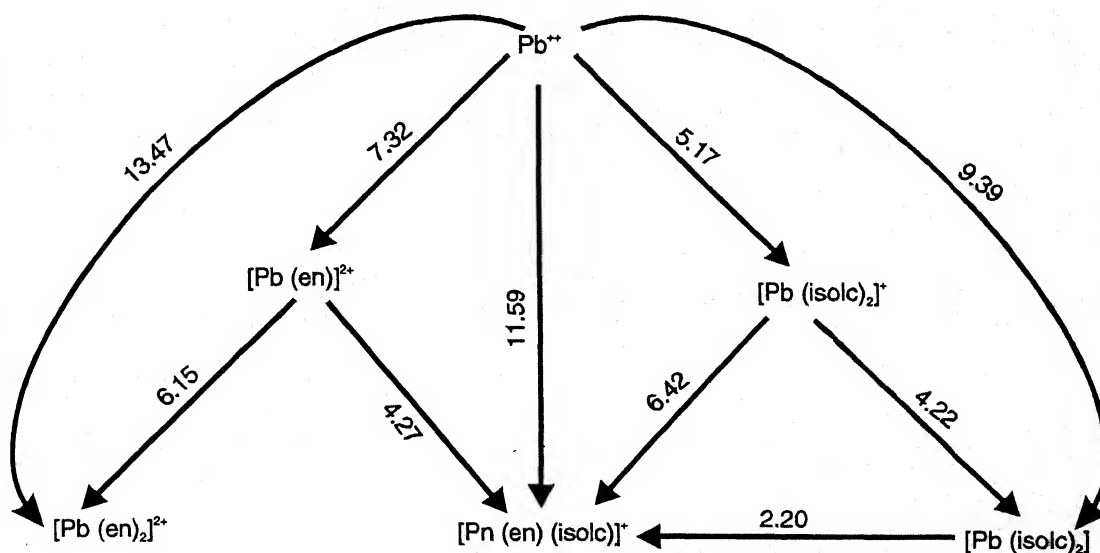
FLWSHEET DIAGRAM - 4.02

LEAD - ETHYLENEDIAMINE - ALANINE SYSTEM



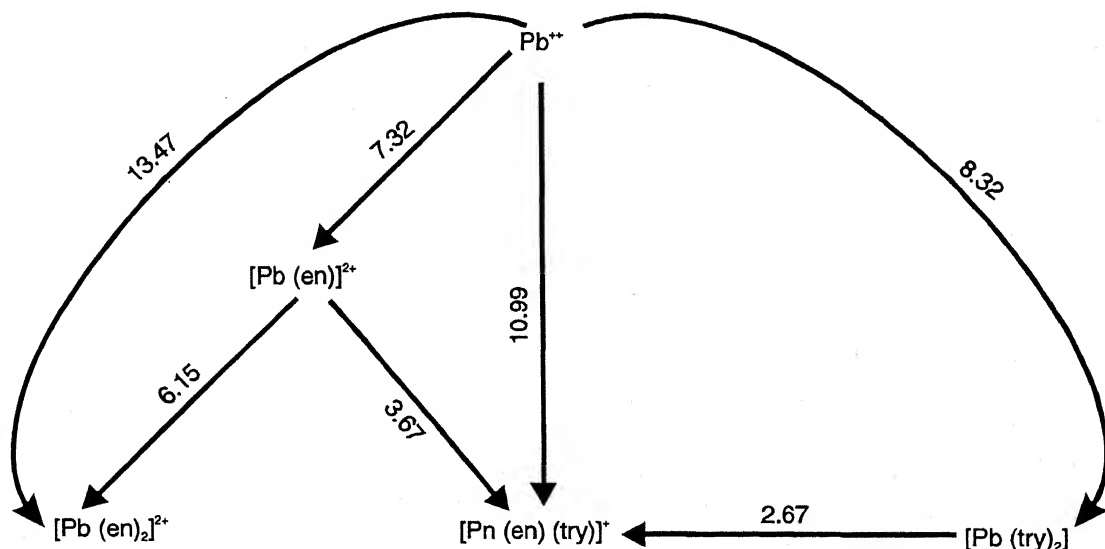
FLWSHEET DIAGRAM - 4.03

LEAD - ETHYLENEDIAMINE - VALINE SYSTEM



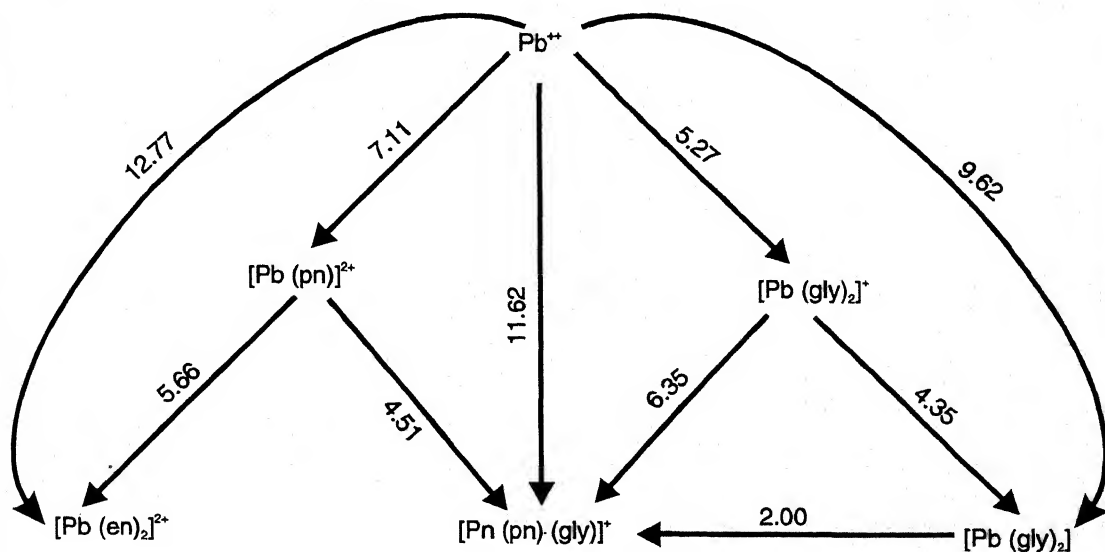
FLWSHEET DIAGRAM - 4.04

LEAD - ETHYLENEDIAMINE - ISOLEUCINE SYSTEM



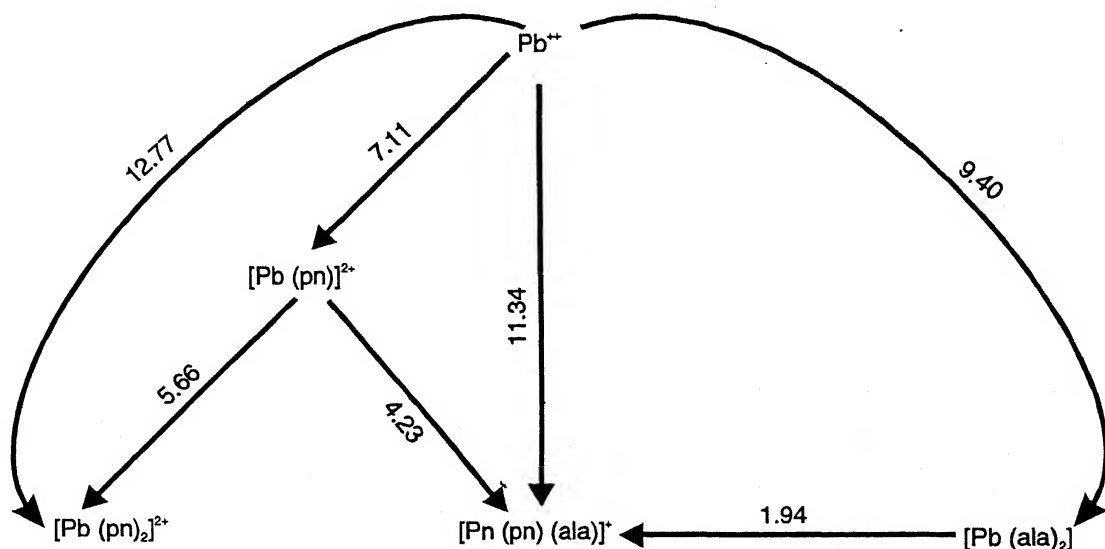
FLWSHEET DIAGRAM - 4.05

LEAD - ETHYLENEDIAMINE - TRYPTOPHAN SYSTEM



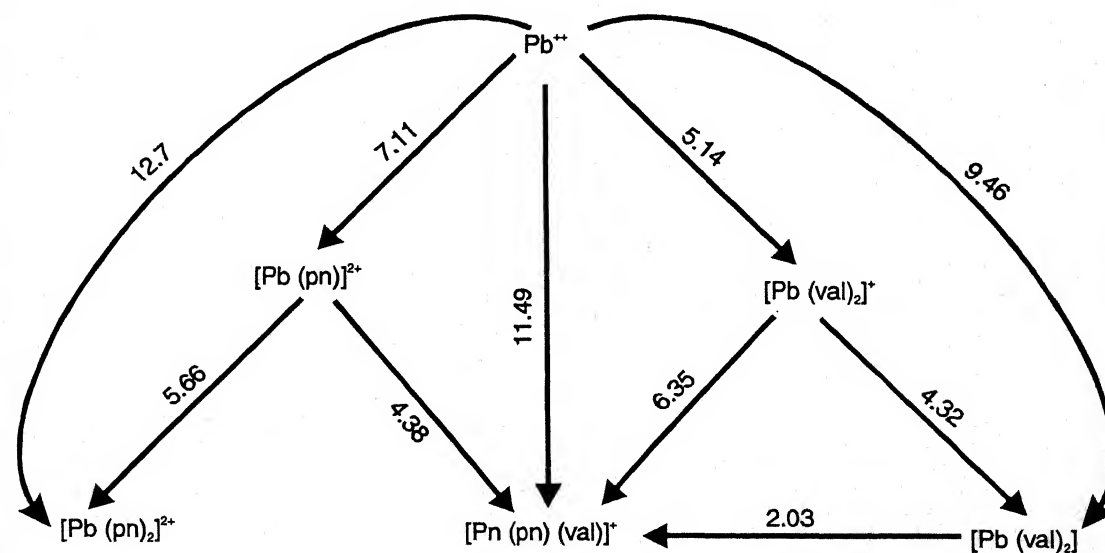
FLWSHEET DIAGRAM - 4.06

LEAD - PROPYLENEDIAMINE - GLYCINE SYSTEM



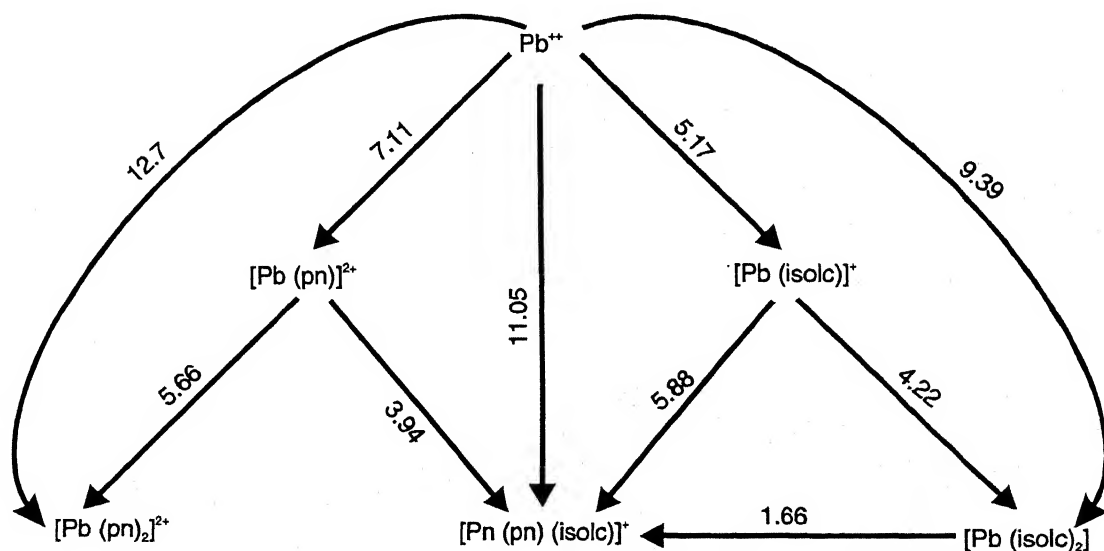
FLWSHEET DIAGRAM - 4.07

LEAD - PROPYLENEDIMINE - ALANINE SYSTEM



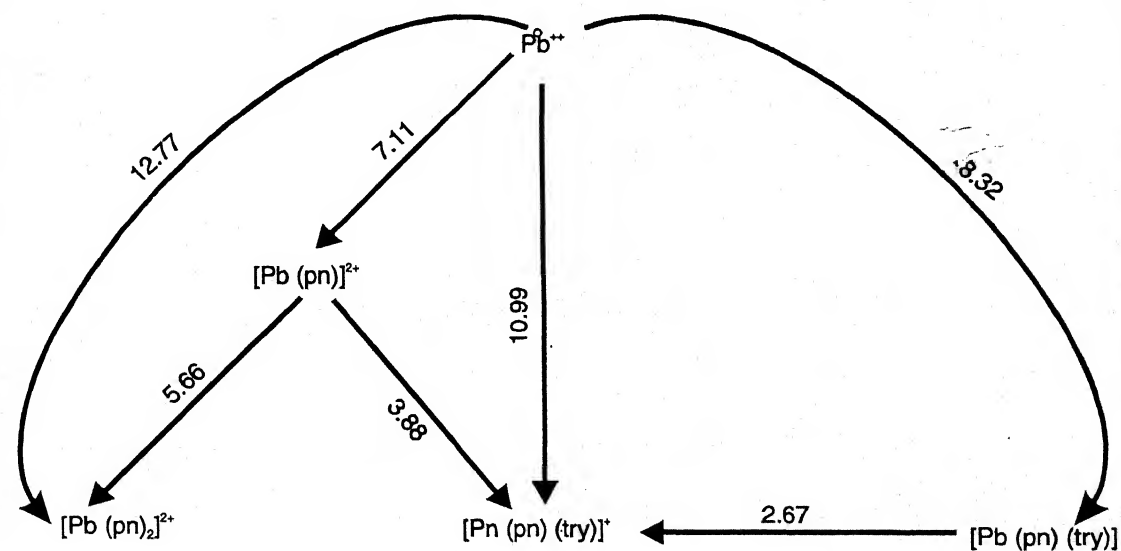
FLWSHEET DIAGRAM - 4.08

LEAD - PROPYLENEDIAMINE - VALINE SYSTEM



FLWSHEET DIAGRAM - 4.09

LEAD - PROPYLENEDIMINE - ISOLEUCINE SYSTEM



FLWSHEET DIAGRAM - 4.10

LEAD - PROPYLENEDIAMINE - TRYPTOPHAN SYSTEM

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CHAPTER - V

COPPER

COMPLEXES

5.01 INTRODUCTION :

Among the metal ions being investigated, Cu (II) forms the strongest complexes. The Cu (II) mixed complexes with ethylenediamine and oxalate ions were studied by Schaap and Mc Masters¹. Later Sunderesan and Sundaram² studied the glycine and α - alanine mixed complex with the metal ion. Saxena and coworkers³ reduced the ternary Cu (II) complexes of pyridoxine and some amino acids at the DME. The co-ordination number of Cu (II) being 4, at the most 1 : 1 : 1 complex could be reported in each case. Alaejos and co-workers⁴ carried out polarographic investigations of Cu (II) complex with glycine and isoleucine. Only one complex was formed. Similarly a number of investigations⁵⁻²⁰ have been carried out on ternary complexes of Cu (II) with amino acids and other ligands.

But it is, obvious that the polarographic investigations of mixed Cu (II) complexes with diamines and amino acids are difficult to locate as not much work has been done in the field. In order to fill this gap, the investigations reported in this chapter were undertaken. The following systems were studied.

- (a) Cu (II) - ethylenediamine - glycine
- (b) Cu (II) - ethylenediamine - DL - alanine
- (c) Cu (II) - ethylenediamine - DL - valine
- (d) Cu (II) - ethylenediamine - L - isoleucine
- (e) Cu (II) - propylenediamine - glycine
- (f) Cu (II) - propylenediamine - DL - alanine
- (g) Cu (II) - propylenediamine - DL - valine and
- (h) Cu (II) - propylenediamine - L - isoleucine

5.02 EXPERIMENTAL

Only the analytical reagent grade chemicals were used. Double distilled water was used to prepare and dilute solutions. Sodium nitrate was used to maintain ionic strength constant at 1.0 M. Triton X - 100 ($2 \times 10^{-3}\%$) was added to every test solution as maxima was observed for the systems under investigation. As described in chapter II, the concentration of the ligand was increased while keeping the ionic strength and pH constant and the polarograms of the test solutions recorded. All measurements were made at $25 \pm 0.1^\circ\text{C}$. Readings were corrected for iR drop.

Capillary characteristics of the DME were as follows $m = 2.40$ mg/sec., $t = 3.10$ sec., at $h_{\text{corr}} = 52.4$ Cm.

The pH of the test solutions was adjusted by adding requisite amounts of dilute NaOH or HCl using a Toshniwal, Cl - 49 pH meter.

n , the number of electrons involved in reduction at DME of Cu (II) in presence of difference ligands was determined as already described²¹ in chapter II. In each and every case, the value of n was found to be 2.

5.03 RESULTS AND DISCUSSION

5.03.01 DETERMINATION OF pKa VALUES

The procedure for determination of pKa values of the ligands has already been described in chapter III.

Table 5.01 to 5.14 contain the experimental data for the simple and ternary complexes system of Cu (II).

5.03.02 NATURE OF POLAROGRAPHIC WAVES

In each and every case Cu (II) gave a well defined polarographic wave in varying concentration of ethylenediamine (en), propylenediamine (pn), glycine (gly), DL - alanine (ala), DL - valine (val) and L - isoleucine (isolc) present singly or in combination. In each case the reduction was found to be entirely diffusion controlled as borne out by the linear nature of i_d vs $h^{1/2}_{corr}$ plots and their passing through the origin.

The reduction in each case was also found to be reversible an inference²² drawn from the linearity of plots of $\log i/i_d - i$ vs E_{de} with slopes of the order of 31 ± 2 mv.

5.03.03 COMPOSITION AND STABILITY OF SIMPLE COMPLEXES

It was deemed essential to determine the composition and stability constants of simple complexes of copper (II) with ethylenediamine (en), propylenediamine (pn), glycine (gly), DL - alanine (ala), DL - valine (val) and L - isoleucine (isolc) seperately before their mixed ligand complexes were investigated. However, identical conditions were maintained for both simple and mixed complex system.

Solution containing 1.0×10^{-3} M Cu (II), 0.1 M en and also 1.0×10^{-3} Cu (II), 0.1 M pn and ionic strength of 1.0 (NaNO_3) were polarographically examined at varing pH. There was a perceptible change in $E_{1/2}$ with change in pH. It was observed that $E_{1/2}$ was maximum at pH 6.60 for both the ligands. It was for this reason that this pH was selected to study the simple as well as mixed complexes. Obviously OH^- are unable to complete with en and pn to enter the coordination sphere.

Tables 5.01 to 5.06 contain the polarographic data of simple Cu

(II) - en, Cu (II) - pn, Cu (II) - gly, Cu (II) - ala, Cu (II) - val, and Cu (II) - isolc systems. In each case, there is a cathodic shift as well as decrease in a diffusion with increase in ligand concentration (fig. 5.01 to 5.06). It indicates complex formation. Except in the case of Cu (II) - val and Cu (II) - isolc system, the plot of $\log [\text{ligand}]$ vs $E_{1/2}$ are smooth curves indicating successive complex formation. Hence the method of DeFord and Hume²³ was applied to determine the stability of two successive complexes in each case (fig. 5.07 to 5.16).

In the case of Cu (II) - val and Cu (II) - isolc, however, the $\log [\text{val}]$ and $\log [\text{isolc}]$ vs $E_{1/2}$ plots separately yield a straight line (fig. 5.23 and 5.24). Hence formation of only one complex was concluded. Its composition and stability was determined by Lingane's method²⁴.

The composition and stability constants of complexes so obtained are summarised below

System	Composition	Stability	Constant
		$\log \beta_1$	$\log \beta_2$
Cu (II) - en	1 : 1, 1 : 2	14.20	20.46
Cu (II) - pn	1 : 1, 1 : 2	14.60	20.32
Cu (II) - gly	1 : 1, 1 : 2	12.27	15.54
Cu (II) - ala	1 : 1, 1 : 2	12.25	15.43
Cu (II) - val	____, 1 : 2	____	15.45
Cu (II) - isolc	____, 1 : 2	____	15.48

5.03.04 COMPOSITION AND STABILITY OF MIXED COMPLEXES

In order to determine the composition and stability constant of mixed ligand complexes, a ligand displacement technique was used and the

method of Schaap and Mc Masters¹ applied. In these mixed ligand systems too, the reduction was found to be reversible involving 2 electrons and was entirely diffusion controlled (fig. 5.17 to 5.24).

(A) Cu (II) - ETHYLENEDIAMINE - GLYCINE SYSTEM

During the investigation of mixed ligand formation in this system, the [gly] was kept constant at 0.1 M and 0.2 M respectively while concentration of ethylenediamine increases from 0.0 to 0.10 M in both the series. The half wave potential values exhibited a greater cathodic shift in presence of glycine than that in its absence each case at each [en] (Table 5.01 and 5.07). It indicated mixed ligand complex formation of Cu (II) with ethylenediamine and glycine.

The computation of values of F_{ij} [X,Y] functions at the two concentrations of glycine (table 5.07) lead to the calculation of the constants A, B and C (as shown in fig. 5.25).

[gly]	log A	log B	log C
0.1 M	9.30	14.71	20.47
0.2 M	9.47	14.81	20.47

The one mixed ligand complex formed had the following composition and stability.

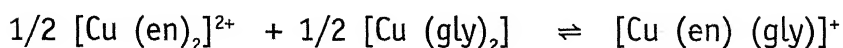


This result broken up into various equilibria is represented in flowsheet diagram 5.01. The numerical figures stand for the logarithm values of equilibria involved.

The equation

$$\log K_M = \log \beta_{11} - 1/2 (\log \beta_{20} + \log \beta_{02})$$

can be used to evaluate the mixing constant K_M of the equilibrium.



It has been found to be + 0.18 for the system. A positive value of K_M is indicative of greater stability of the mixed complex $[\text{Cu} (\text{en}) (\text{gly})_2]^+$ over simple $[\text{Cu} (\text{en})_2]^{2+}$ and $[\text{Cu} (\text{gly})_2]$ complexes. For the following disproportionation reaction



the equilibrium constant is - 0.36. The negative value is once again suggestive of greater stability of mixed ligand complex over simple binary complex.

(B) Cu (II) - ETHYLENEDIAMINE - DL - ALANINE SYSTEM

During the investigation of mixed ligand formation in this system, the $[\text{ala}]$ was kept constant at 0.1 M and 0.2 M respectively while concentration of ethylenediamine increased from 0.0 to 0.10 M in both the series. The half wave potential values exhibited a greater cathodic shift in presence of alanine than that in its absence in each case at each $[\text{en}]$ (Table 5.01 and 5.08). It indicated mixed ligand complex formation of Cu (II) with ethylenediamine and alanine. The computations of $F_{ij}(X,Y)$ functions lead to the following values of the constants A, B and C (vide fig. 5.26).

$[\text{ala}]$	$\log A$	$\log B$	$\log C$
0.1 M	9.00	14.74	20.47
0.2 M	9.30	14.90	20.49

The one mixed ligand complex formed had the following composition and stability :

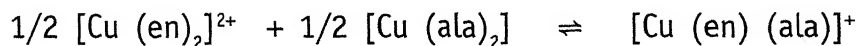


This result broken up into various equilibria is represented in flowsheet Diagram 5.02. The numerical figures stand for the logarithm values of equilibria involved.

The equation

$$\log K_M = \log \beta_{11} - 1/2 (\log \beta_{20} + \log \beta_{02})$$

can be used to evaluate the mixing constant K_M of the equilibrium.



It has been found to be + 0.71 for the system. A positive value of K_M is indicative of greater stability of the mixed complex $[\text{Cu (en) (ala)}]^+$ over simple $[\text{Cu (en)}_2]^{2+}$ and $[\text{Cu (ala)}_2]$ complexes.

For the following disproportionation reactions



the equilibrium constant is - 1.43. The negative value is once again suggestive of greater stability of mixed ligand complex over simple binary complexes.

(C) Cu (II) - ETHYLENEDIAMINE - DL - VALINE SYSTEM

During the investigation of mixed ligand formation in this system, the [val] was kept constant at 0.1 M and 0.2 M respectively while concentration of ethylenediamine increased from 0.0 to 0.10 M in both the series. The half wave potential values exhibited a greater cathodic shift in presence of valine than that in its absence in each case at each [en] (Table 5.01 and 5.09). It indicated mixed complex formation of Cu (II) with ethylenediamine and valine. The computation of values of F_{ij} [X,Y] functions at the two concentrations of valine (Table 5.09) lead to the calculation of the constant A, B and C as depicted in fig. 5.27.

[val]	log A	log B	log C
0.1 M	9.74	14.87	20.50
0.2 M	5.95	14.92	20.51

The one mixed ligand complex formed had the following composition and stability.

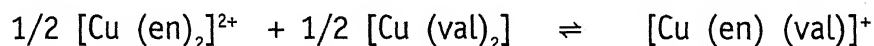
$$[\text{Cu (en) (val)}]^+ : \log \beta_{11} = 18.12$$

This result broken up into various equilibria is represented in flowsheet diagram 5.03. The numerical figure stand for the logarithm values of equilibria involved.

The equation

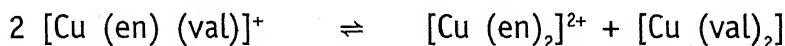
$$\log K_m = \log \beta_{11} - 1/2 (\log \beta_{20} + \log \beta_{02})$$

can be used to evaluate the mixing constant K_m of the equilibrium



It has been found to be + 0.16 for the system. A positive value of K_m is indicative of greater stability of the complex $[\text{Cu (en) (val)}]^+$ over simple $[\text{Cu (en)}_2]^{2+}$ and $[\text{Cu (val)}_2]$ complexes.

For the following disproportionation reaction



the equilibrium constant is - 0.33. The negative value is once again suggestive of greater stability of mixed ligand complex over simple binary complexes.

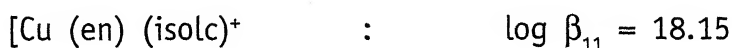
(D) Cu (II) - ETHYLENEDIAMINE - L - ISOLEUCINE SYSTEM

During the investigation of mixed ligand formation in this system, the [isolc] was kept constant at 0.1 M and 0.2 M respectively while concentration of ethylenediamine increased from 0 to 0.10 M in both the

series. The half wave potential values exhibited a greater cathodic shift in presence of isoleucine than that in its absence in each case at each [en] (Table 5.01 and 5.10). It indicated complex formation of Cu (II) with ethylenediamine and isoleucine simultaneously. The computation of F_{ij} [X,Y] functions at the two concentrations of isoleucine (Table 5.10) lead to the calculation of the constant A, B and C (fig. 5.28).

[isolec]	log A	log B	log C
0.1 M	9.30	14.87	20.49
0.2 M	9.60	14.92	20.47

The only mixed ligand complex formed had the following composition and stability

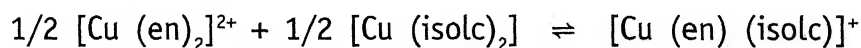


The result broken up into various equilibria is represented in flowsheet Diagram 5.04. The numerical figures stand for the logarithm values of equilibria involved.

The equation

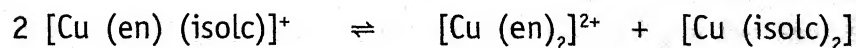
$$\log K_M = \log \beta_{11} - 1/2 (\log \beta_{20} + \log \beta_{02})$$

can be used to evaluate the mixing constant K_M of the equilibrium



It has been found to be + 0.18 for the system. A positive value of K_M is indicative of greater stability of the mixed complex $[\text{Cu}(\text{en})(\text{isolec})]^+$ over simple $[\text{Cu}(\text{en})_2]^{2+}$ and $[\text{Cu}(\text{isolec})_2]$ complexes.

For the following disproportionation reaction



the equilibrium constant is - 0.36. The negative value is once

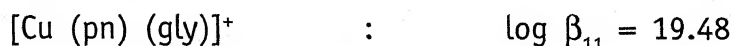
again suggestive of greater stability of mixed ligand complex over simple binary complex.

(E) Cu (II) - PROPYLENEDIAMINE - GLYCINE SYSTEM

During the investigation of mixed ligand formation in this system, the [gly] was kept constant at 0.1 M and 0.2 M respectively while concentration of propylenediamine increased from 0.0 to 0.10 M in both the series. The half wave potential values exhibited greater cathodic shift in presence of glycine than that in its absence in each case at each [pn] (Table 5.02 and 5.11). It indicated mixed complex formation of Cu (II) with propylenediamine and glycine. The computation of glycine of F_{ij} [X,Y] functions at the two concentrations of glycine (Table 5.11) lead to the calculation of the constant A, B and C. It is clearly depicted in fig. 5.29.

[gly]	log A	log B	log C
0.1 M	9.47	14.77	20.47
0.2 M	9.60	14.90	20.50

The one mixed ligand complex formed had the following composition and stability

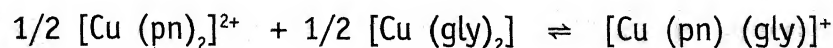


The result broken up into various equilibria is represented in flowsheet diagram 5.05. The numerical figures stand for the logarithm values of equilibria involved.

The equation

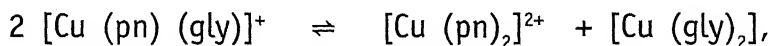
$$\log K_M = \log \beta_{11} - 1/2 (\log \beta_{20} + \log \beta_{02})$$

can be used to evaluate the mixing constant K_M of the equilibrium



It has been found to be 0.55 for the system. A positive value of K_M is indicative of greater stability of the mixed complex $[\text{Cu}(\text{pn})(\text{gly})]^+$ over simple $[\text{Cu}(\text{pn})_2]^{2+}$ and $[\text{Cu}(\text{gly})_2]$ complexes.

For the following disproportionation reaction



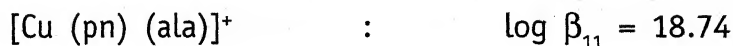
the equilibrium constant is - 1.10. The negative value is once again suggestive of greater stability of mixed ligand complex over simple binary complexes.

(F) Cu - (II) PROPYLENEDIAMINE - DL - ALANINE SYSTEM

During the investigation of mixed ligand formation of this system, the $[\text{ala}]$ was kept constant at 0.1 M and 0.2 M respectively while concentration of propylenediamine increased from 0 to 0.10 M in both the series. The half wave potential values exhibited a greater cathodic shift in presence of alanine than that in its absence in each case at each $[\text{pn}]$ (Table 5.02 and 5.12). It indicated ternary complex formation of Cu (II) with propylenediamine and alanine. The computation of $F_{ij} [X,Y]$ functions at the two concentrations of alanine (Table 5.12) lead to the calculation of the constant A, B and C (fig. 5.30).

$[\text{ala}]$	$\log A$	$\log B$	$\log C$
0.1 M	9.39	14.87	20.50
0.2 M	9.77	14.95	20.51

The one mixed ligand complex formed had the following composition and stability :



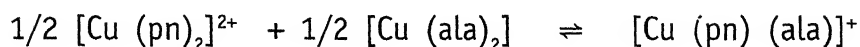
This result broken up into various equilibria is represented in

flowsheet Diagram 5.06. The numerical figures stand for the logarithm values of equilibria involved.

The equation

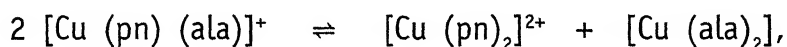
$$\log K_M = \log \beta_{11} - 1/2 (\log \beta_{20} + \log \beta_{02})$$

can be used to evaluate the mixing constant K_M of the equilibrium



It has been found to be + 0.86 for the system. A positive value of K_M is indicative of greater stability of the mixed complex $[\text{Cu (pn) (ala)}]^+$ over simple $[\text{Cu (pn)}_2]^{2+}$ and $[\text{Cu (ala)}_2]$ complexes.

For the following disproportionation reaction



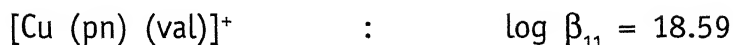
the equilibrium constant is - 1.73. The negative value is once again suggestive of greater stability of mixed ligand complex over simple binary complex.

[G] Cu (II) - PROPYLENEDIAMINE - DL - VALINE SYSTEM

During the investigation of mixed ligand formation in this system, the [val] was kept constant at 0.1 M and 0.2 M respectively while concentration of propylenediamine increased from 0.0 to 0.10 M in both the series. The half wave potential values exhibited a greater cathodic shift in presence of valine than that in its absence in each case at each [pn] (Table 5.02 and 5.13). It indicated complex formation of Cu (II) with propylenediamine and valine. The computation of F_{ij} [X,Y] functions at the two concentrations of valine (Table 5.13) lead to the values of the constants A, B and C. Figure 5.31 illustrated the calculation of these constants.

[val]	log A	log B	log C
0.1 M	9.47	14.70	20.50
0.2 M	9.95	14.95	20.51

The one mixed ligand complex formed had the following composition and stability.

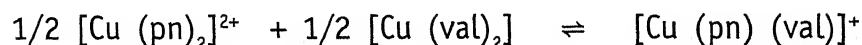


This result broken up into various equilibria is represented in flowsheet diagram 5.07. The numerical figures stand for the logarithm involved.

The equation

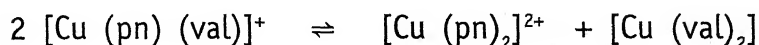
$$\log K_M = \log \beta_{11} - 1/2 (\log \beta_{20} + \log \beta_{02})$$

can be used to evaluate the mixing constant K_M of the equilibrium



It has been found to be + 0.70 and is indicative of greater stability of the mixed complex $[\text{Cu (pn) (val)}]^+$ over simple $[\text{Cu (pn)}_2]^{2+}$ and $[\text{Cu (val)}_2]$ complexes.

For the following disproportionation reaction,



the equilibrium constant is - 1.41. The negative value is once again suggestive of greater stability of mixed ligand complex over simple binary complexes.

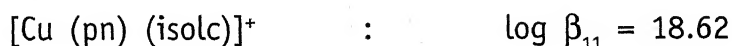
(H) Cu (II) - PROPYLENEDIAMINE - L - ISOLEUCINE SYSTEM

During the investigation of mixed ligand formation in this system, the [isolc] was kept constant at 0.1 M and 0.2 M respectively while concentration of propylenediamine increases from 0.0 M to 0.10 M in both

the series. The half wave potential values exhibited a greater cathodic shift in presence of isoleucine than that in its absence in each case at each [pn] (Table 5.02 and 5.14). It indicated mixed complex formation of Cu (II) with propylenediamine and isoleucine. The computation of F_{ij} [X,Y] functions at the two concentrations of isoleucine (Table 5.14) lead to the calculation of the constant A, B and C (vide fig. 5.32).

[isolc]	log A	log B	log C
0.1 M	9.47	14.69	20.44
0.2 M	9.77	14.90	20.45

The one mixed ligand complex formed had the following composition and stability

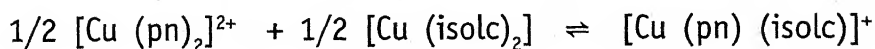


This result brokenup into various equilibria is represented in flowsheet diagram 5.08. The numerical figures stand for the logarithm values of equilibria involved.

The equation

$$\log K_M = \log \beta_{11} - 1/2 (\log \beta_{20} + \log \beta_{02})$$

can be used to evaluate the mixing constant K_M of the equilibrium



It has been found to be + 0.72 for the system. A positive value of K_M is indicative of greater stability of the mixed complex $[\text{Cu (pn) (isolc)}]^+$ over the simple $[\text{Cu (pn)}_2]^{2+}$ and $[\text{Cu (isolc)}_2]$ complexes.

For the following disproportionation reaction



the equilibrium constants is - 1.44. The negative value is once again suggestive of greater stability of mixed complex over simple binary complexes.

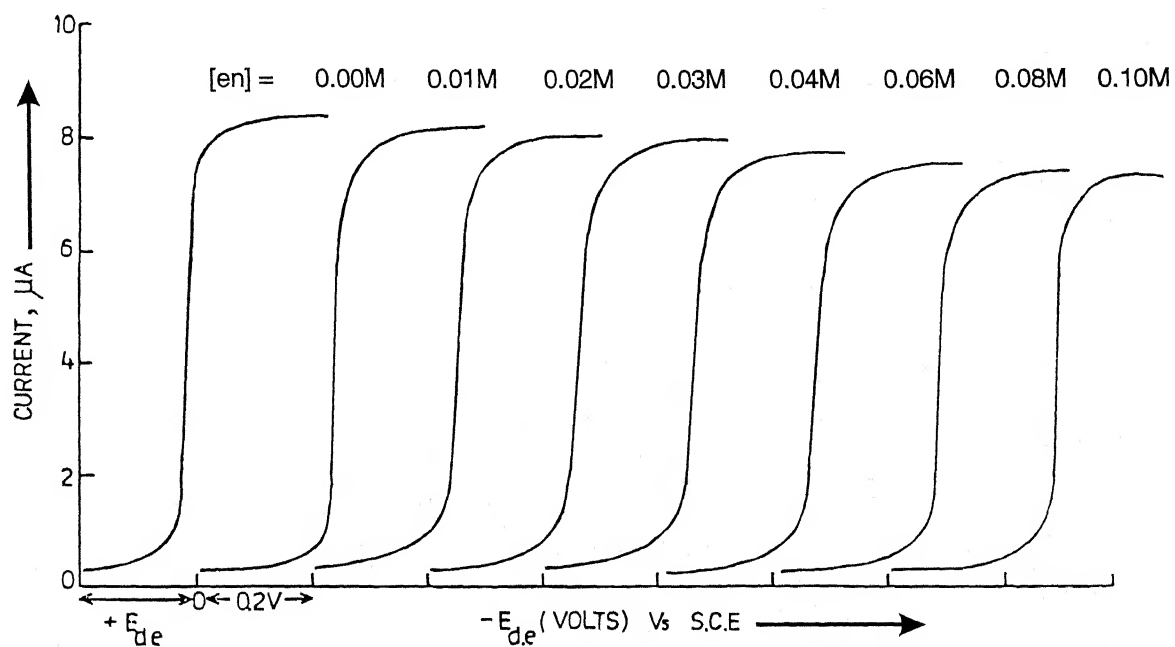


FIG. 5.01 POLAROGRAPHIC WAVES OF Cu(II) - ETHYLENEDIAMINE SYSTEM

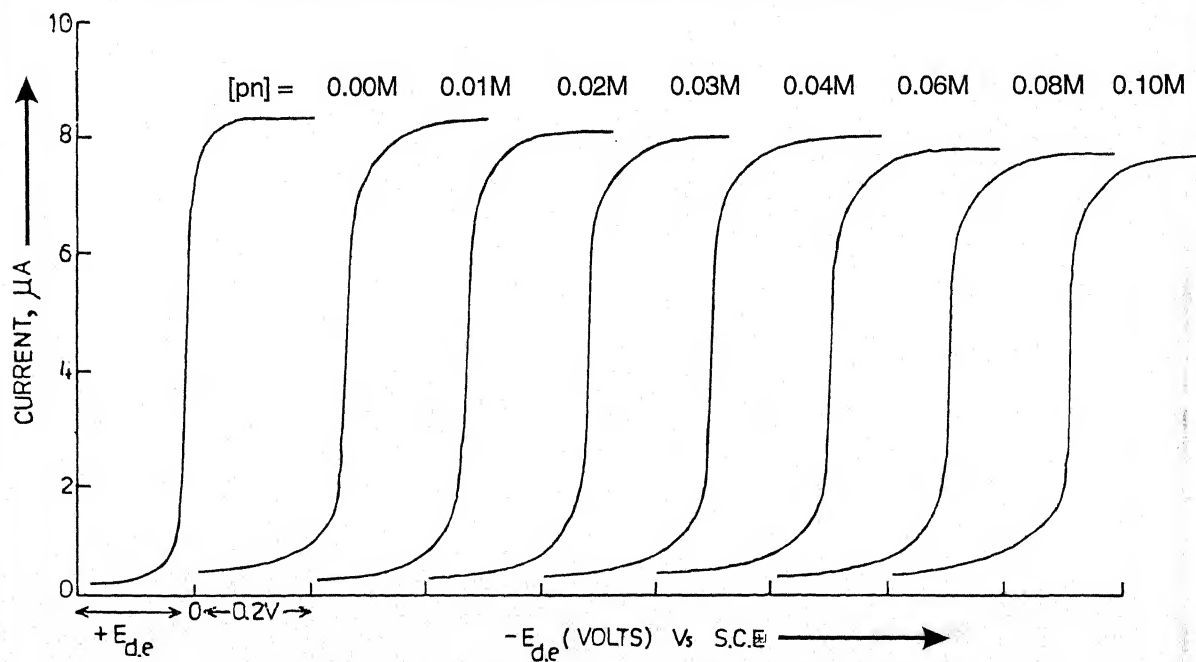


FIG. 5.02 POLAROGRAPHIC WAVES OF Cu(II) - PROPYLENEDIAMINE SYSTEM

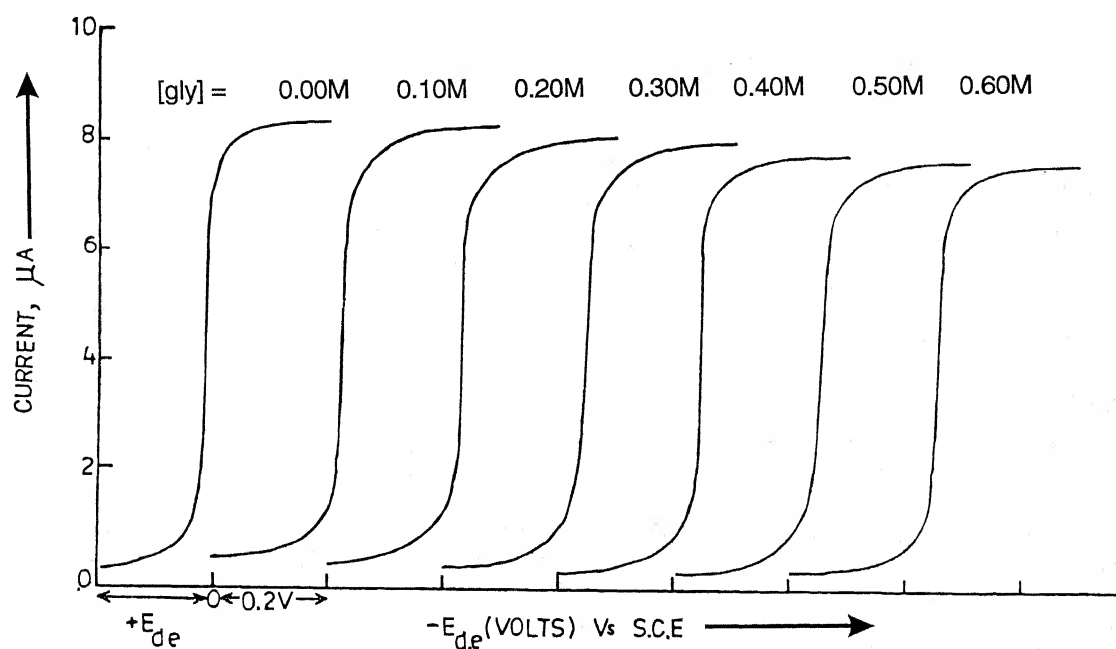


FIG. 5.03 POLAROGRAPHIC WAVES OF Cu (II) - GLYCINE SYSTEM

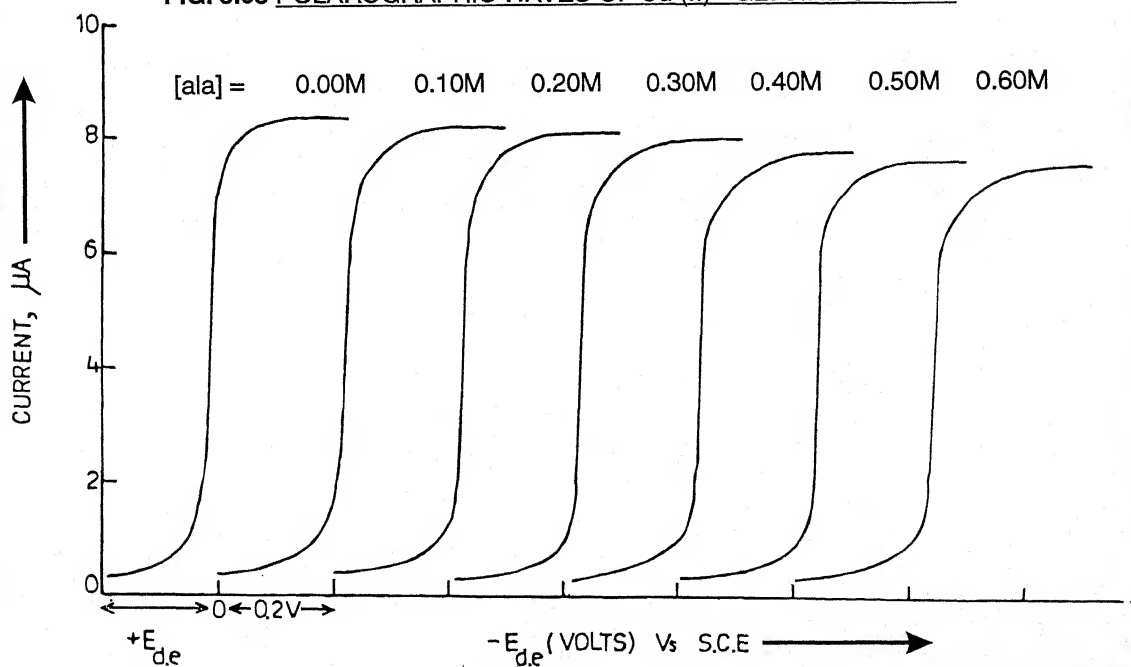


FIG. 5.04 POLAROGRAPHIC WAVES OF Cu (II) - DL - ALANINE SYSTEM

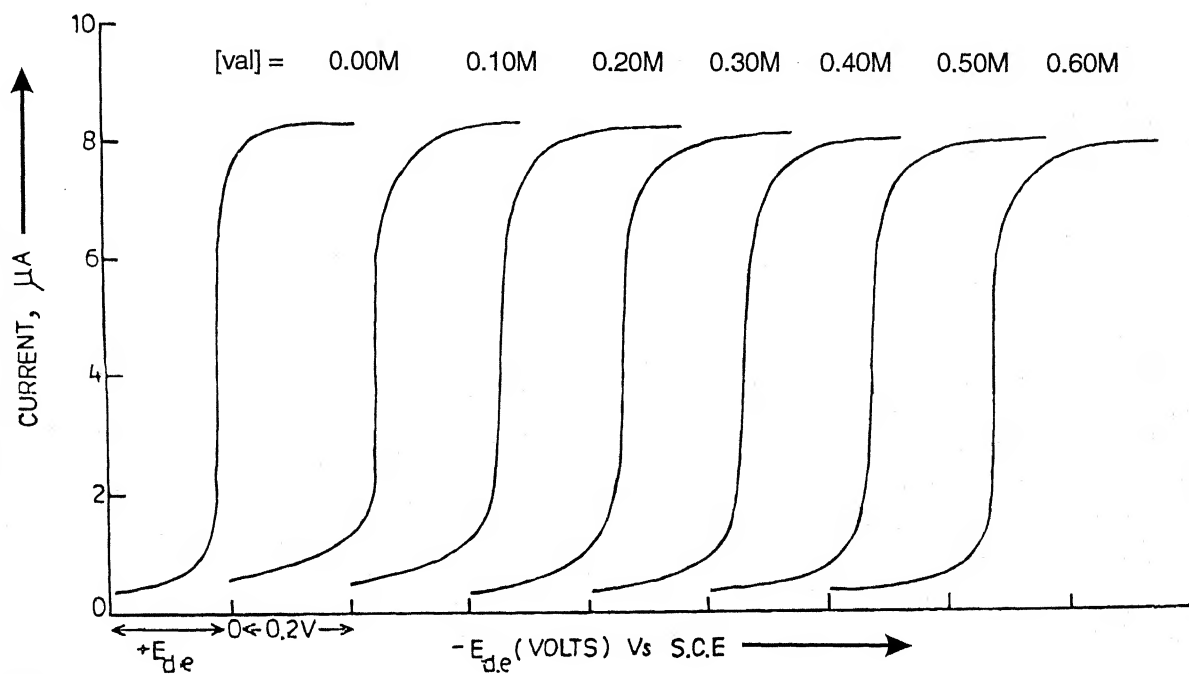


FIG. 5.05 POLAROGRAPHIC WAVES OF Cu(II) - D L - VALINE SYSTEM

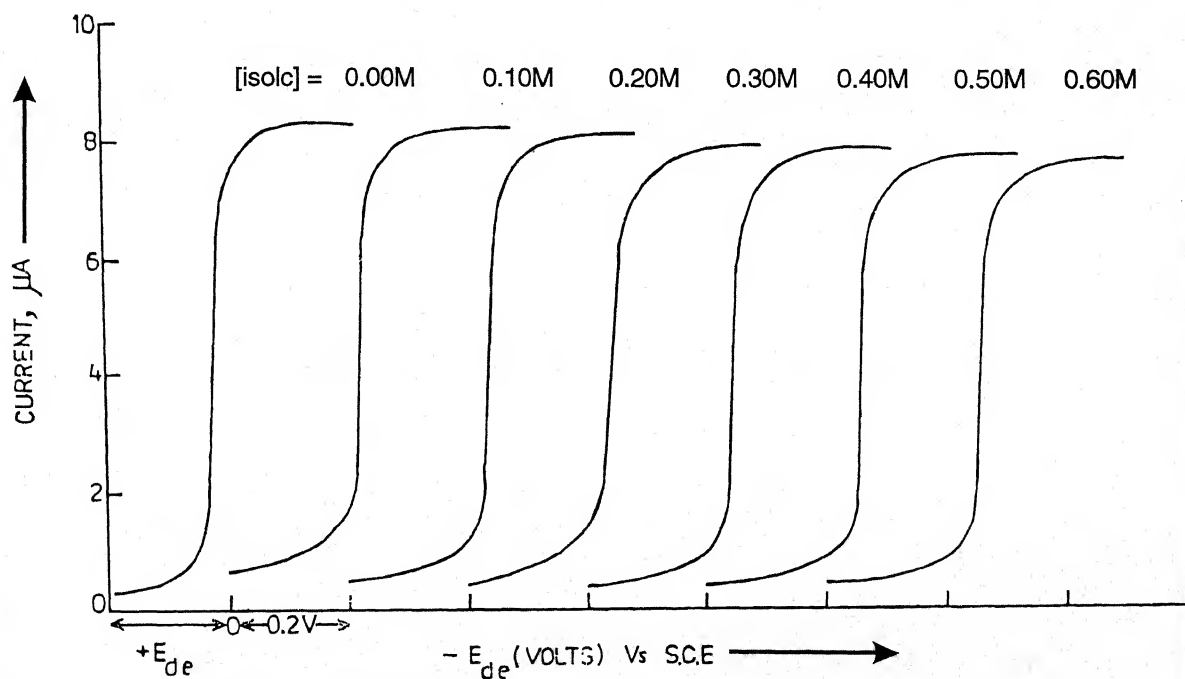


FIG. 5.06 POLAROGRAPHIC WAVES OF Cu(II) - L - ISOLEUCINE SYSTEM

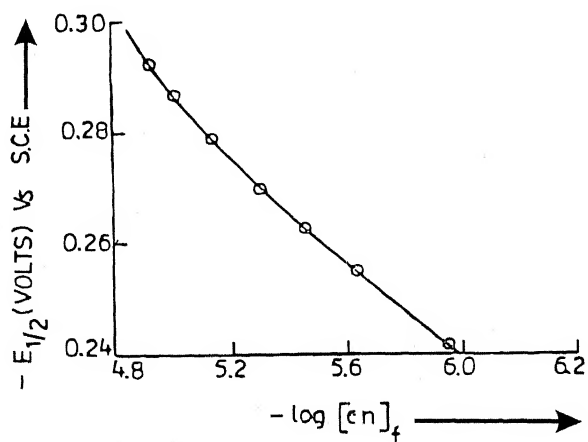


FIG. 5.07 PLOT OF $-E_{1/2}$ Vs $-\log [en]_f$ FOR Cu (II) - ETHYLENEDIAMINE SYSTEM

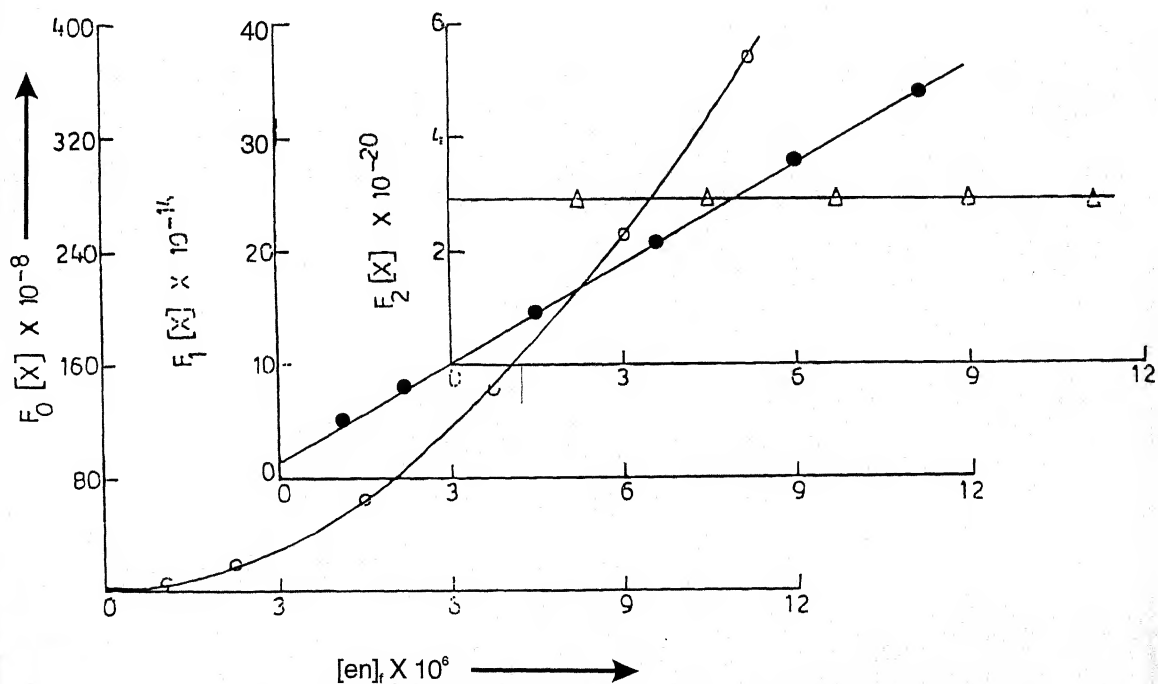


FIG. 5.08 PLOT OF $F_i [X]$ Vs $[en]_f$ FOR Cu (II) - ETHYLENEDIAMINE SYSTEM

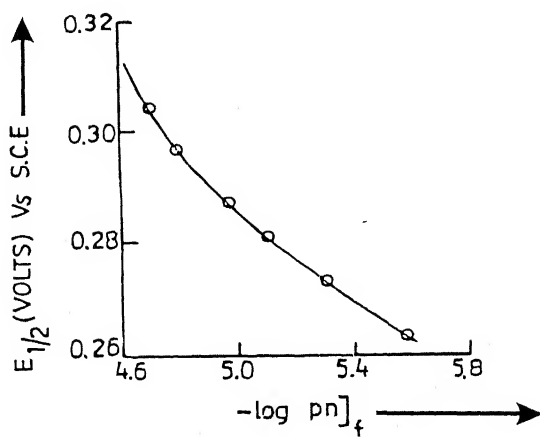


FIG. 5.09 PLOT OF $-E_{1/2}$ Vs $-\log [pn]_f$ FOR Cu (II) - PROPYLENEDIAMINE SYSTEM

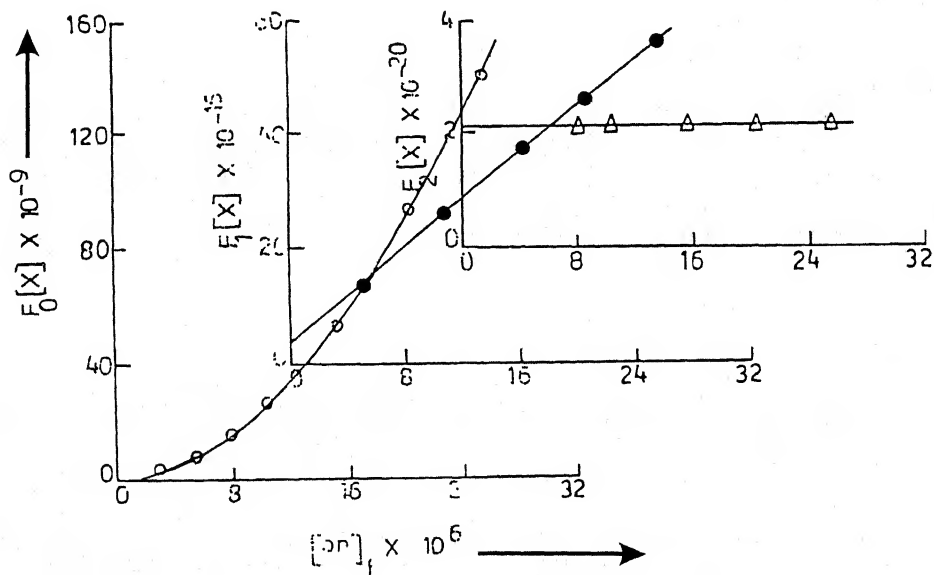


FIG. 5.10 PLOT OF $F_0[X]$ Vs $[pn]_f$ FOR Cu (II) - PROPYLENEDIAMINE SYSTEM

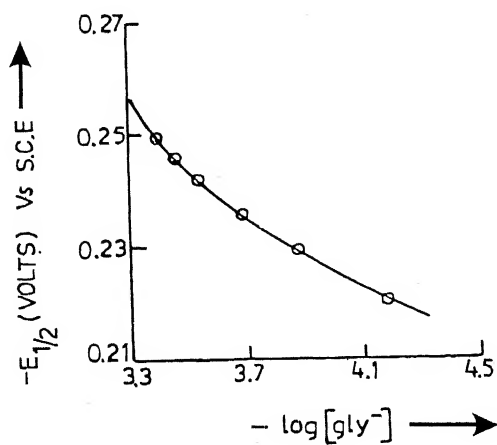


FIG. 5.11 PLOT OF $-E_{1/2}$ Vs $-\log [\text{gly}]$ FOR Cu (II) - GLYCINE SYSTEM

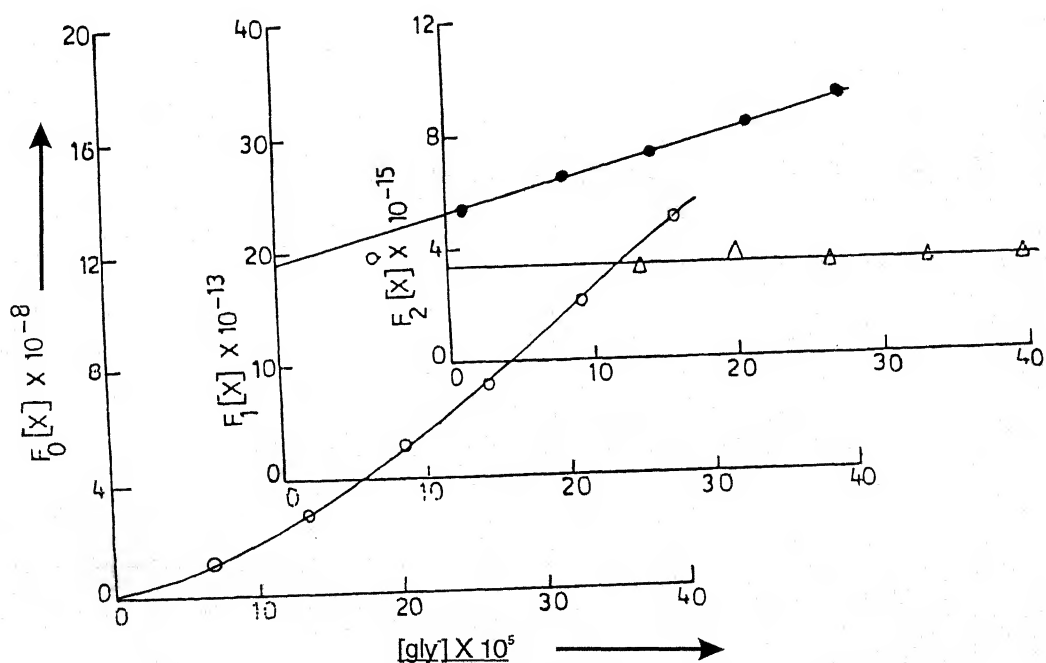


FIG. 5.12 PLOT OF $F_i [X]$ Vs $[\text{gly}]$ FOR Cu (II) - GLYCINE SYSTEM

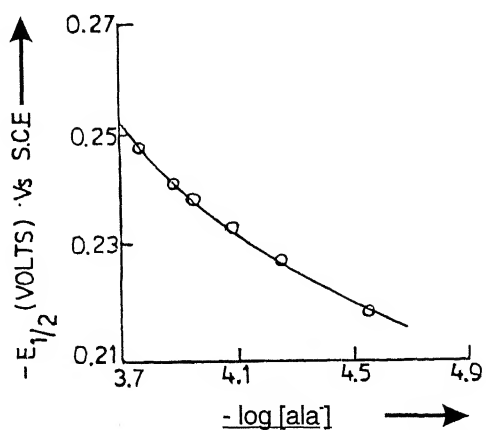


FIG. 5.13 PLOT OF $-E_{1/2}$ Vs $-\log [\text{ala}]$ FOR Cu (II) - DL - ALANINE SYSTEM

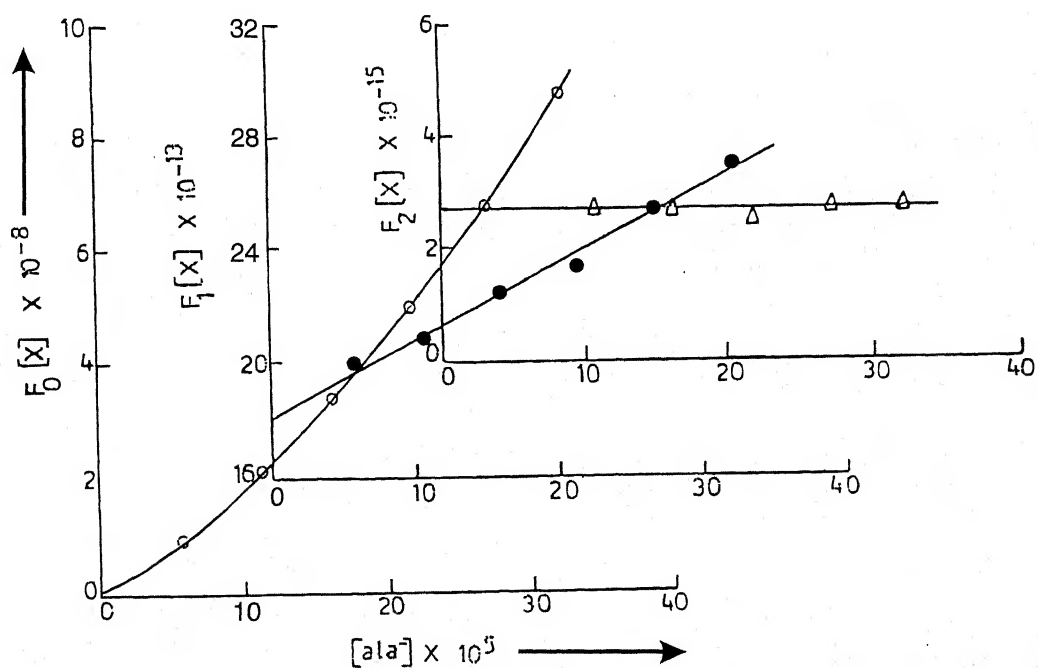


FIG. 5.14 PLOTS OF $F_i[X]$ Vs $[\text{ala}]$ FOR Cu (II) - DL - ALANINE SYSTEM

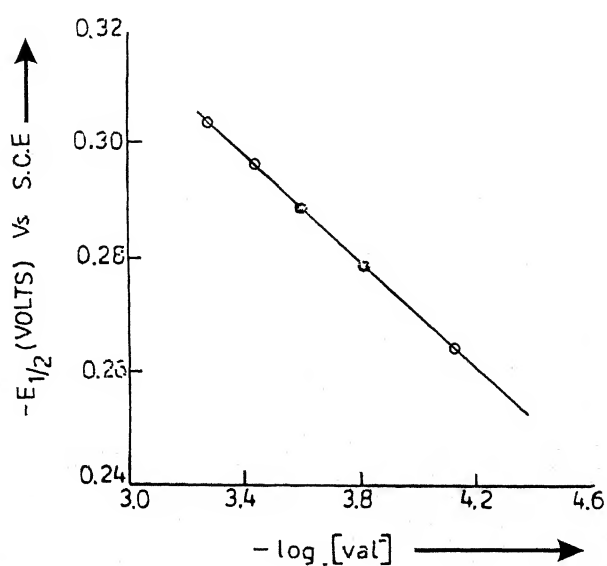


FIG. 5.15 PLOT OF $-E_{1/2}$ Vs $-\log [\text{val}]$ FOR Cu (II) - DL - VALINE SYSTEM

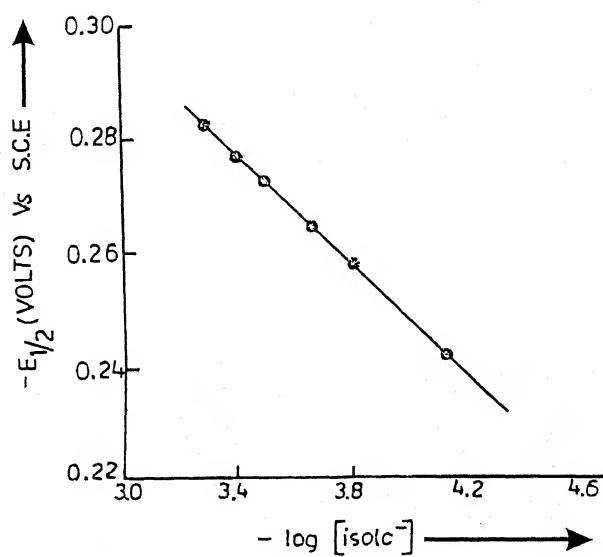


FIG. 5.16 PLOT OF $-E_{1/2}$ Vs $-\log [\text{isoleu}]$ FOR Cu(II) - ISOLEUCINE SYSTEM

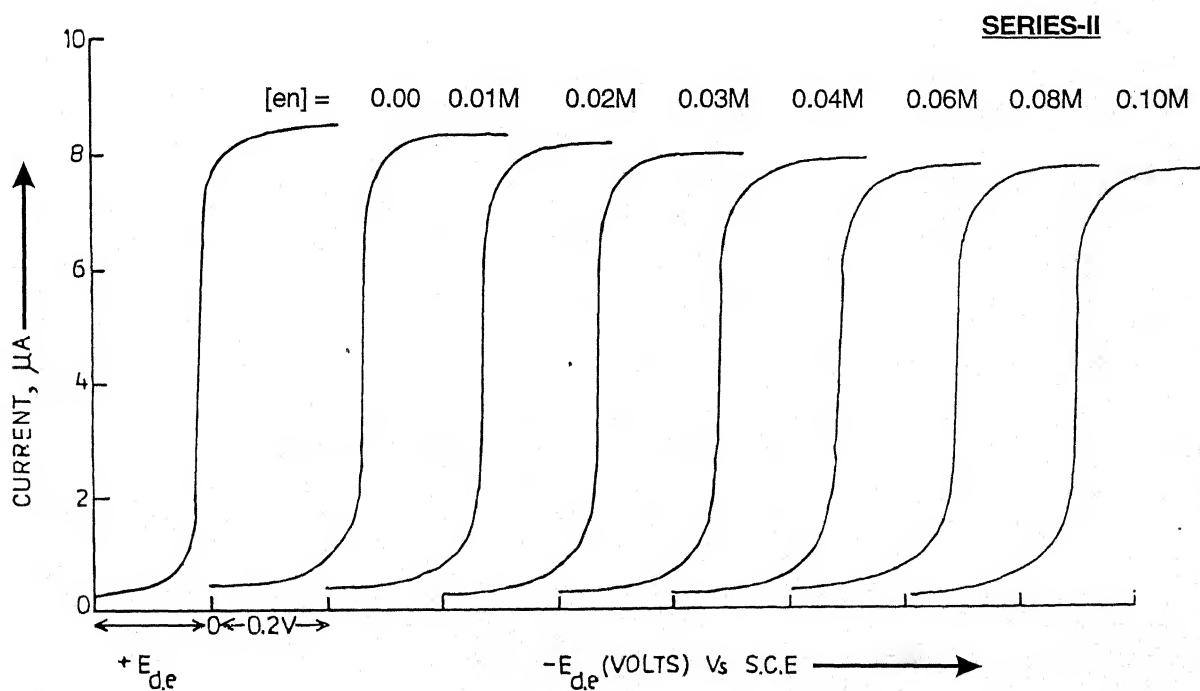
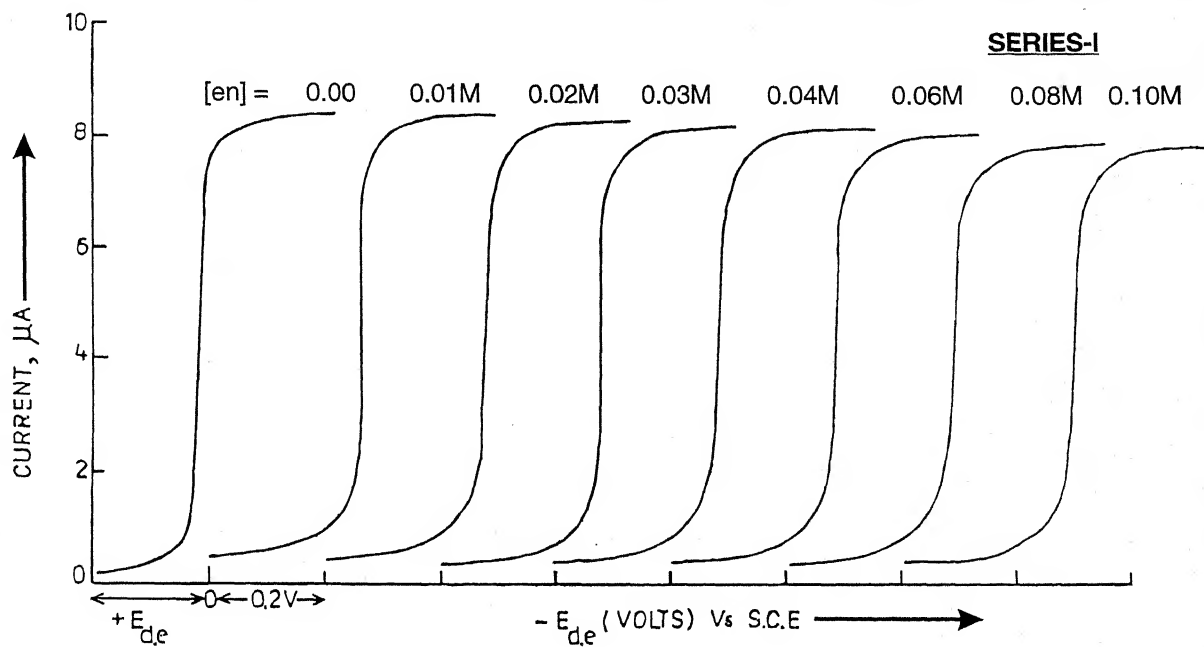


FIG. 5.17 POLAROGRAPHIC WAVES OF Cu (II) - ETHYLENEDIAMINE GLYCINE SYSTEM

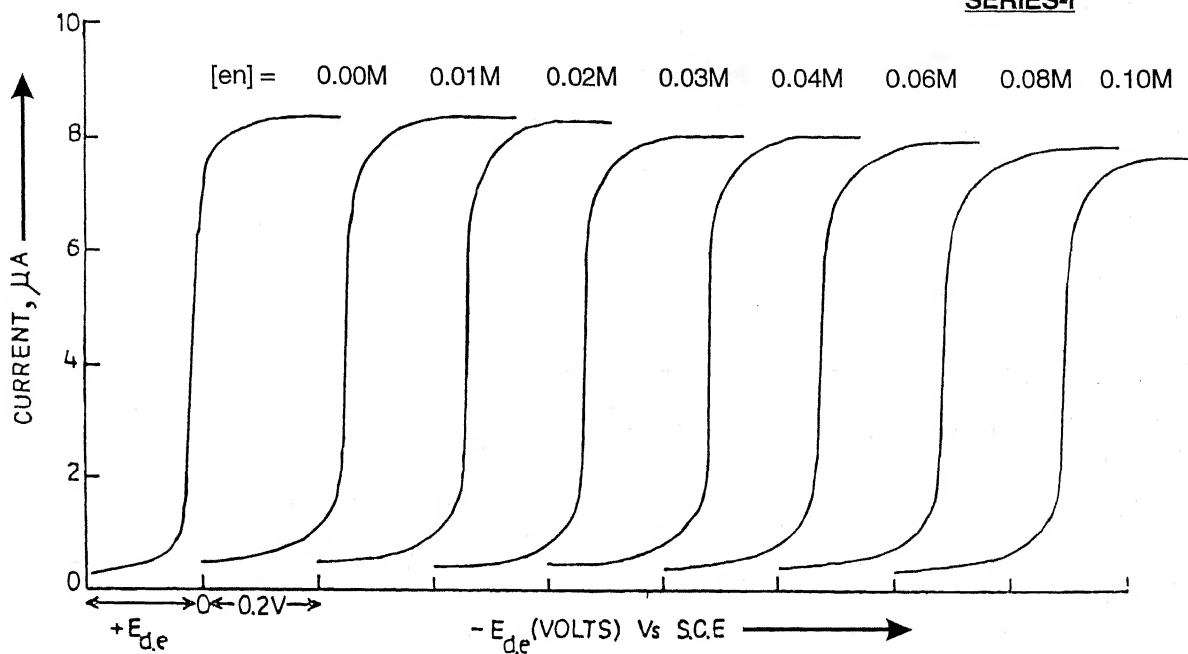
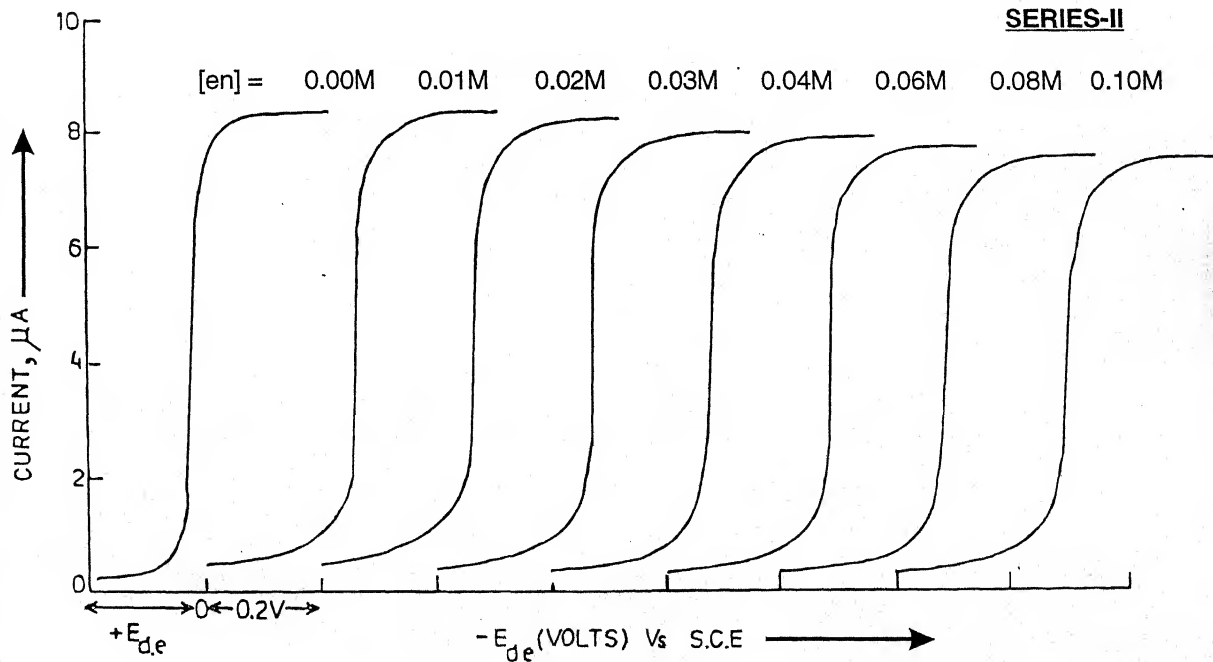
SERIES-I**SERIES-II**

FIG. 5.18 POLAROGRAPHIC WAVES OF Cu(II) - ETHYLENEDIAMINE - DL - ALANINE SYSTEM

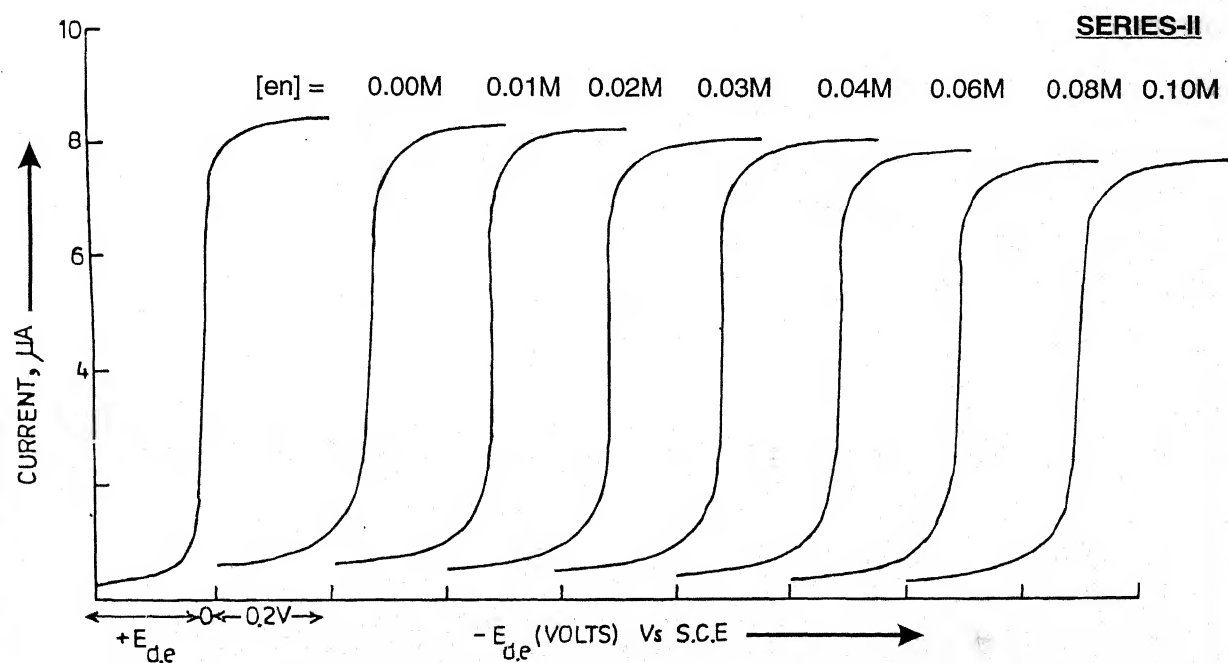
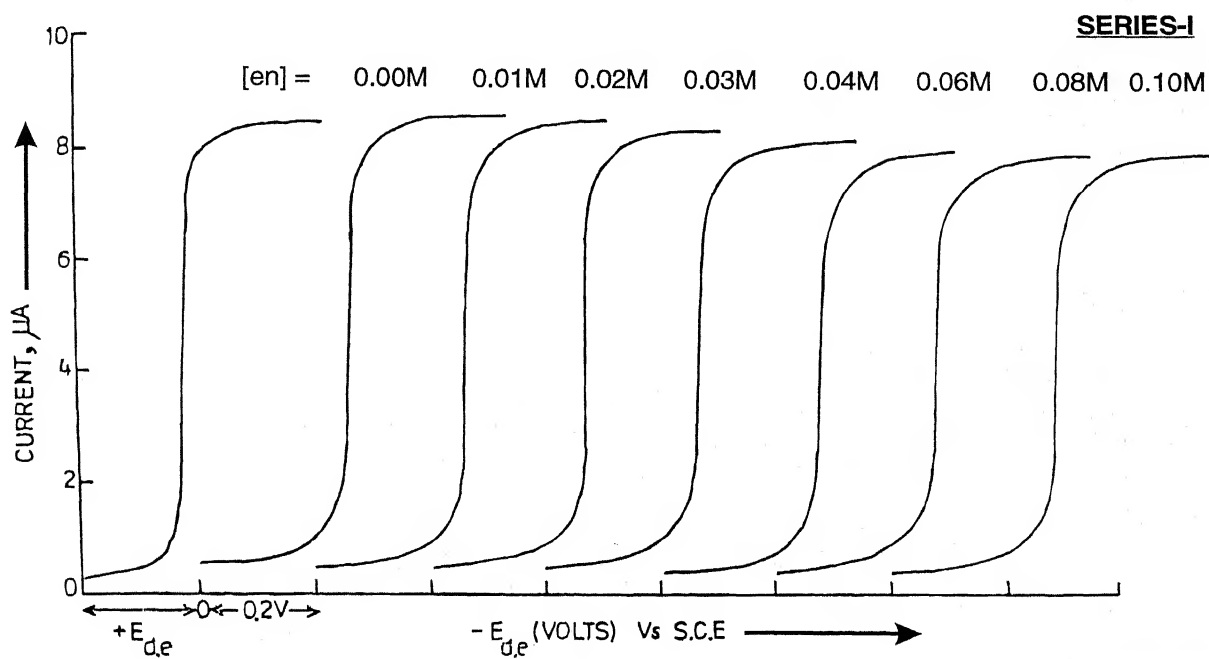


FIG. 5.19 POLAROGRAPHIC WAVES OF Cu (II) - ETHYLENEDIAMINE - DL - VALINE SYSTEM

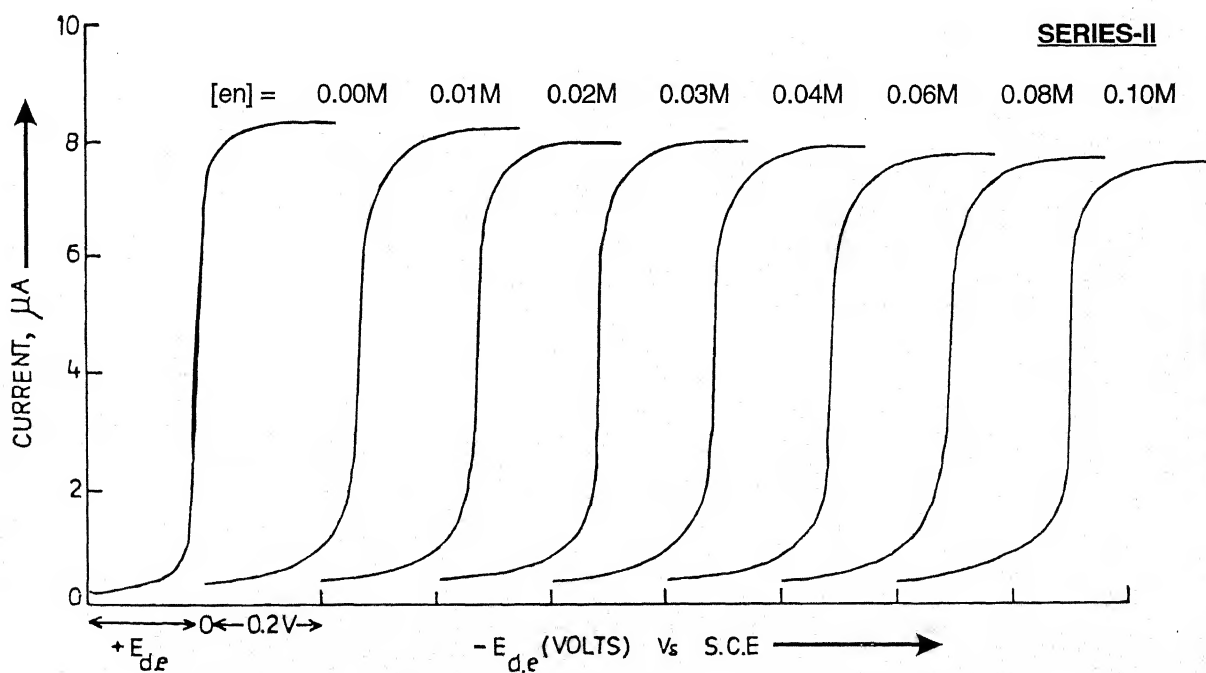
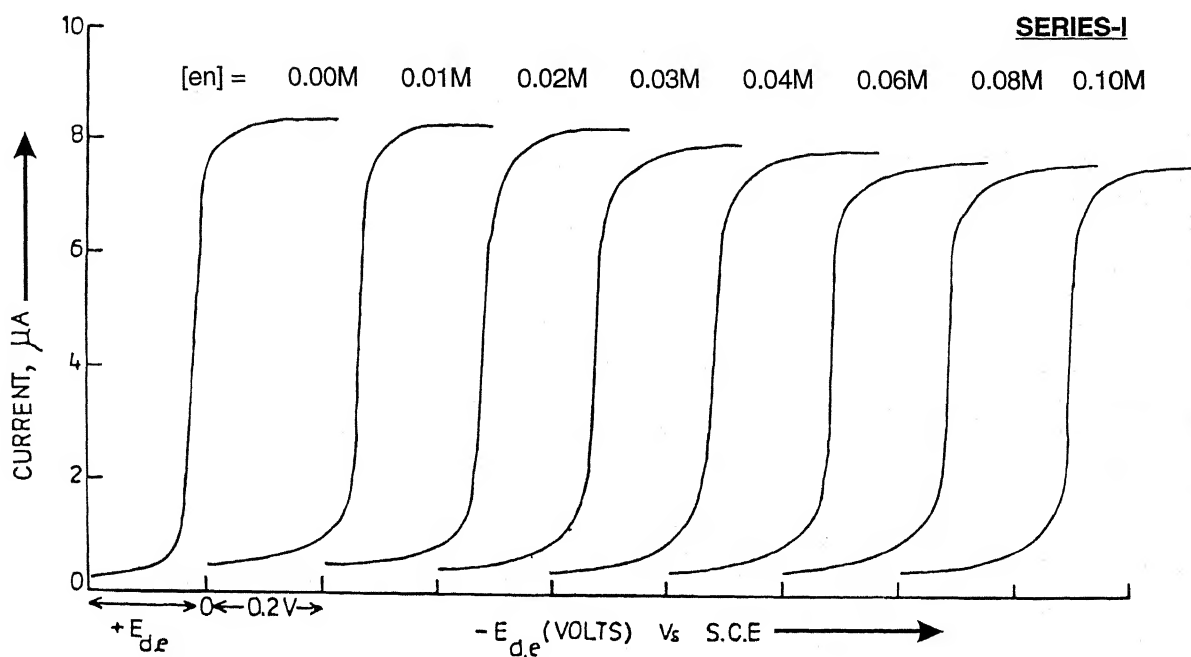


FIG. 5.20 POLAROGRAPHIC WAVES OF Cu (II) - ETHYLENEDIAMINE - L - ISOLEUCINE SYSTEM

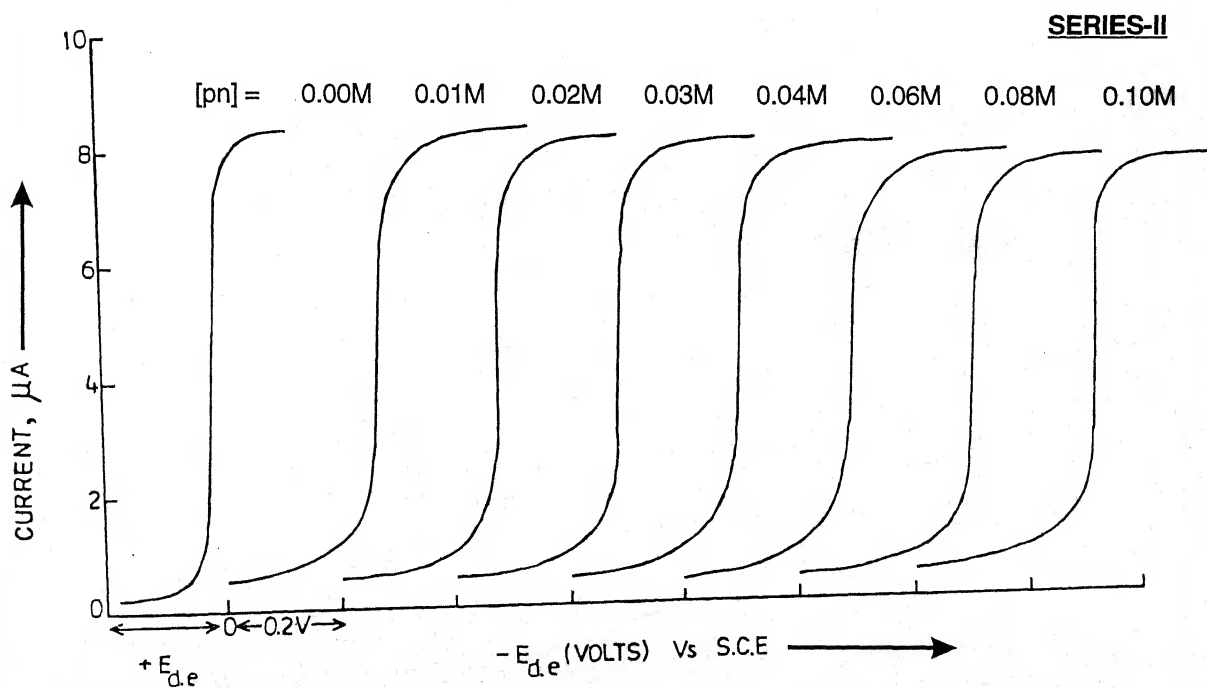
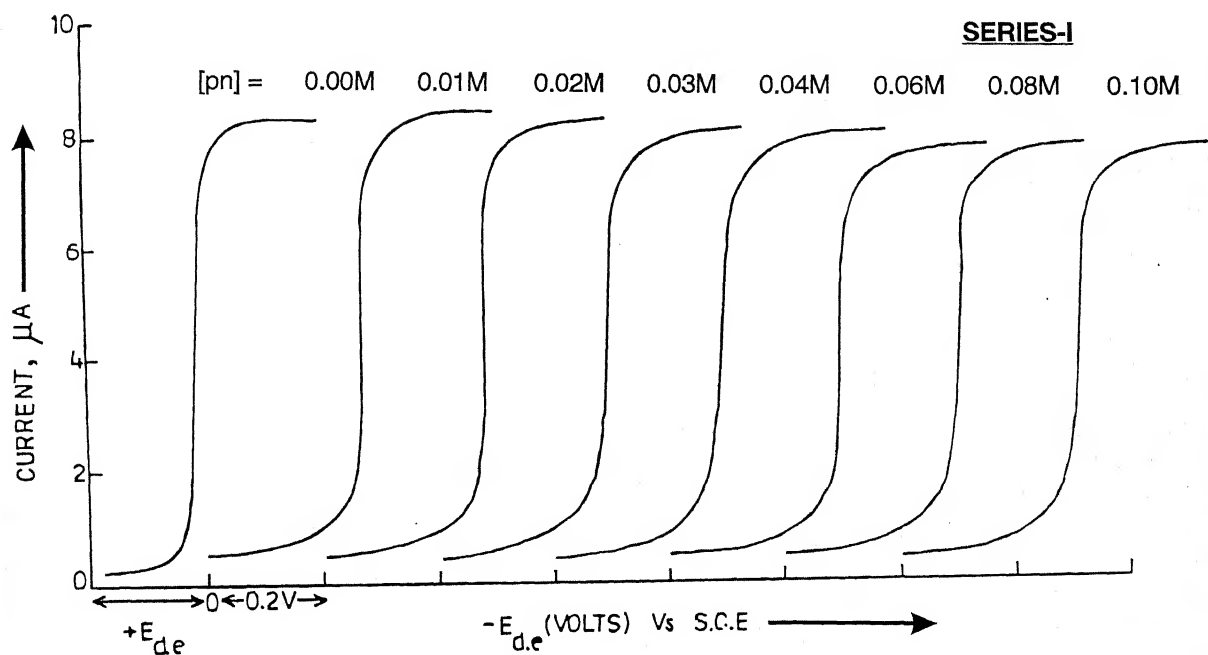
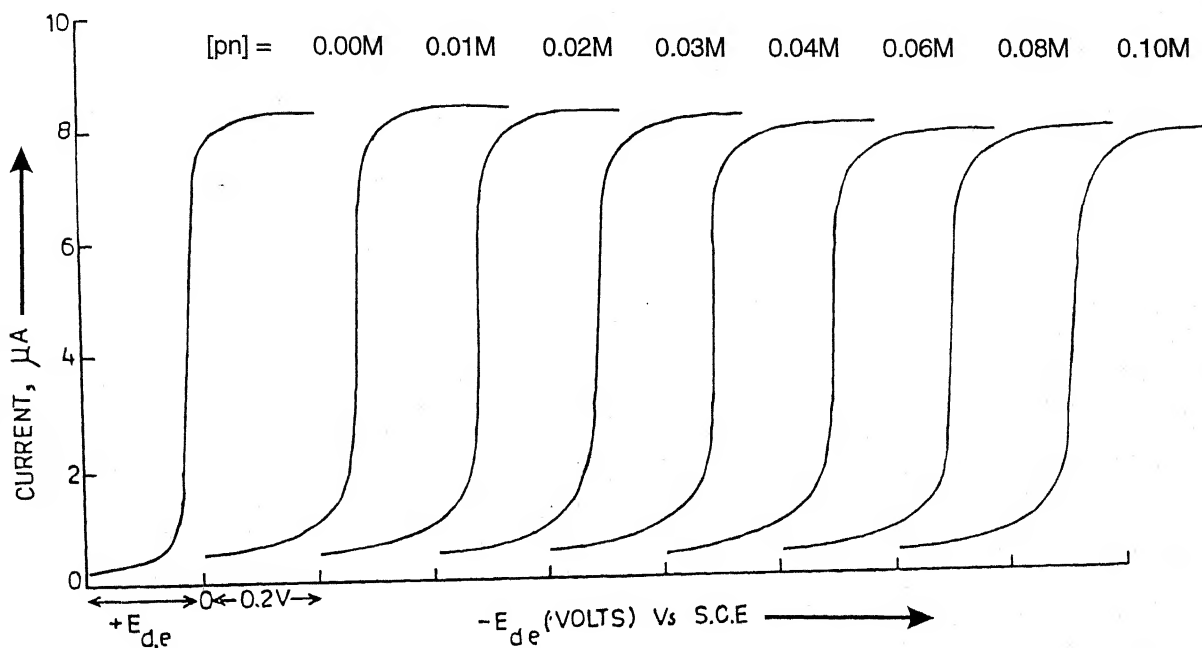
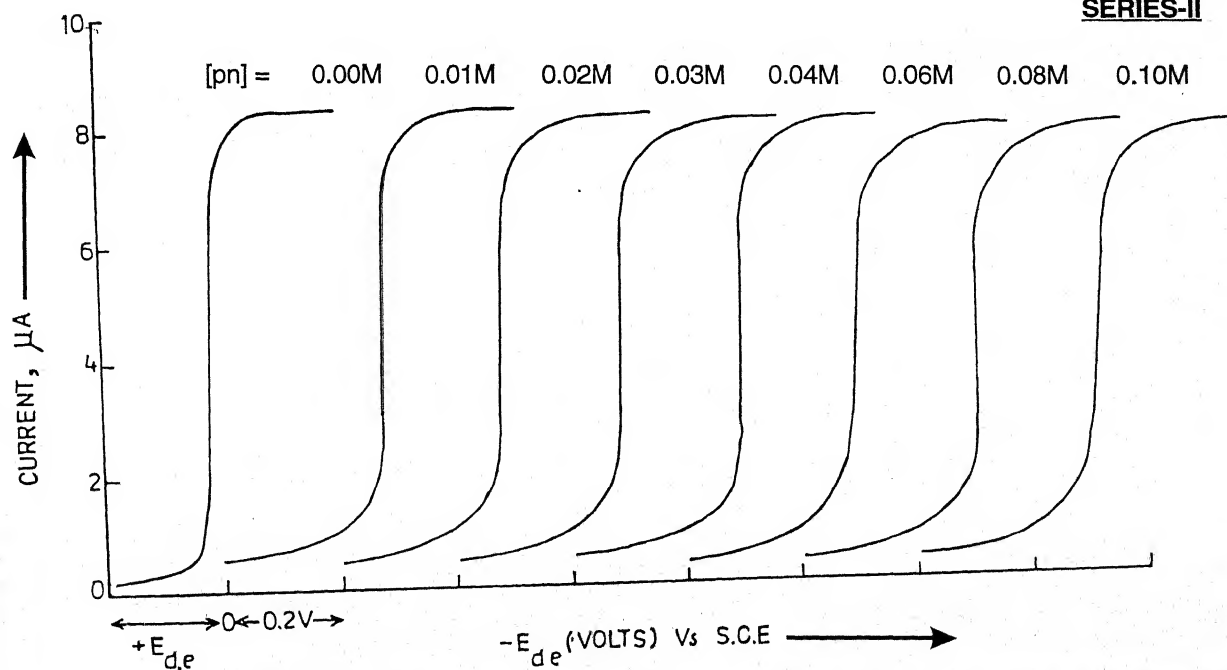


FIG. 5.21 POLAROGRAPHIC WAVES OF Cu (II) - PROPYLENEDIAMINE GLYCINE SYSTEM

SERIES-I**SERIES-II****FIG. 5.22 POLAROGRAPHIC WAVES OF $Cu(II)$ - PROPYLENEDIAMINE - DL - ALANINE SYSTEM**

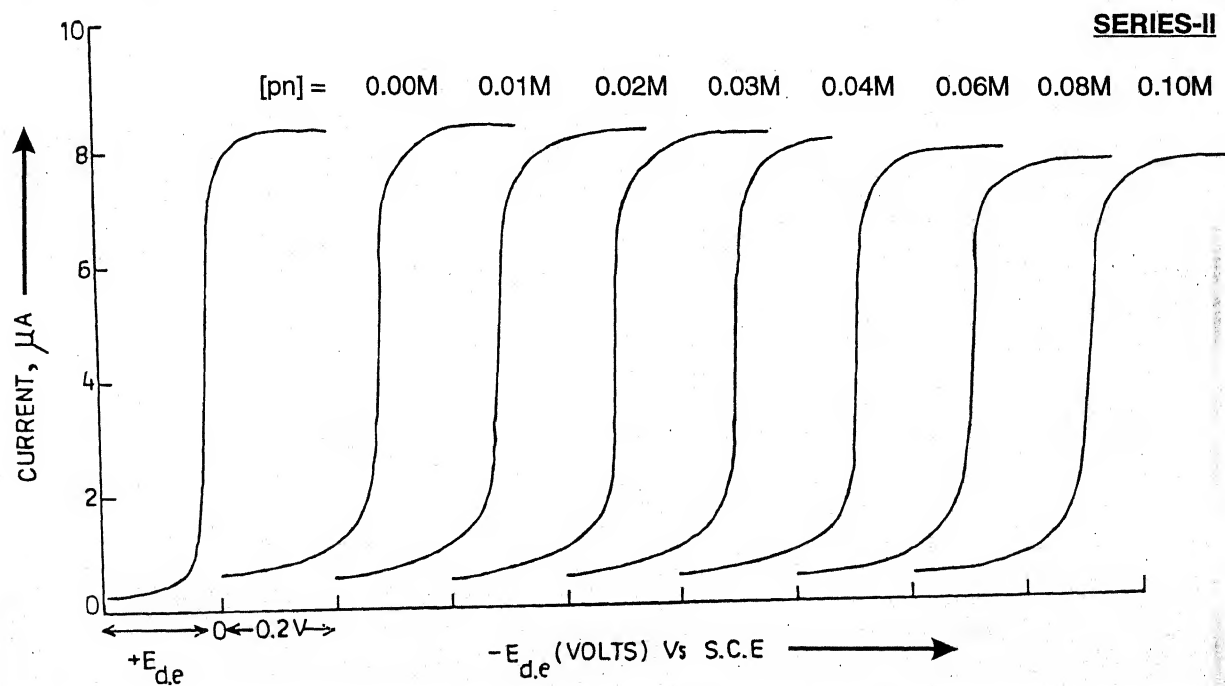
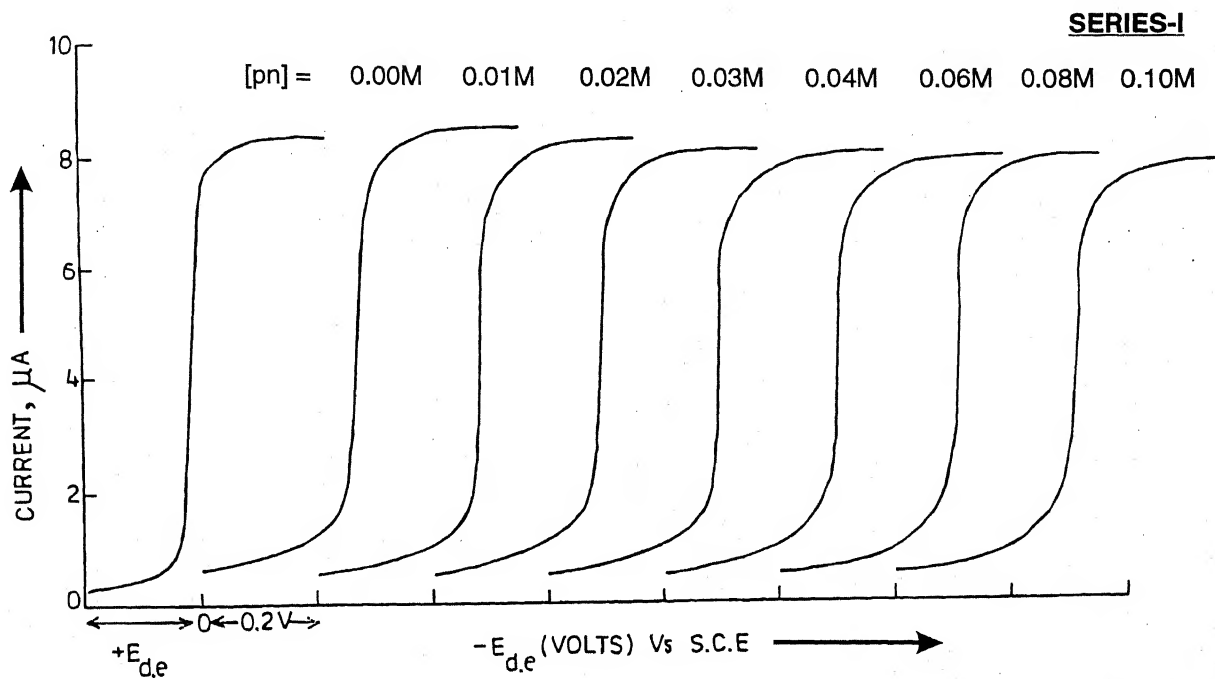


FIG. 5.23 POLAROGRAPHIC WAVES OF Cu (II) - PROPYLENEDIAMINE - DL - VALINE SYSTEM

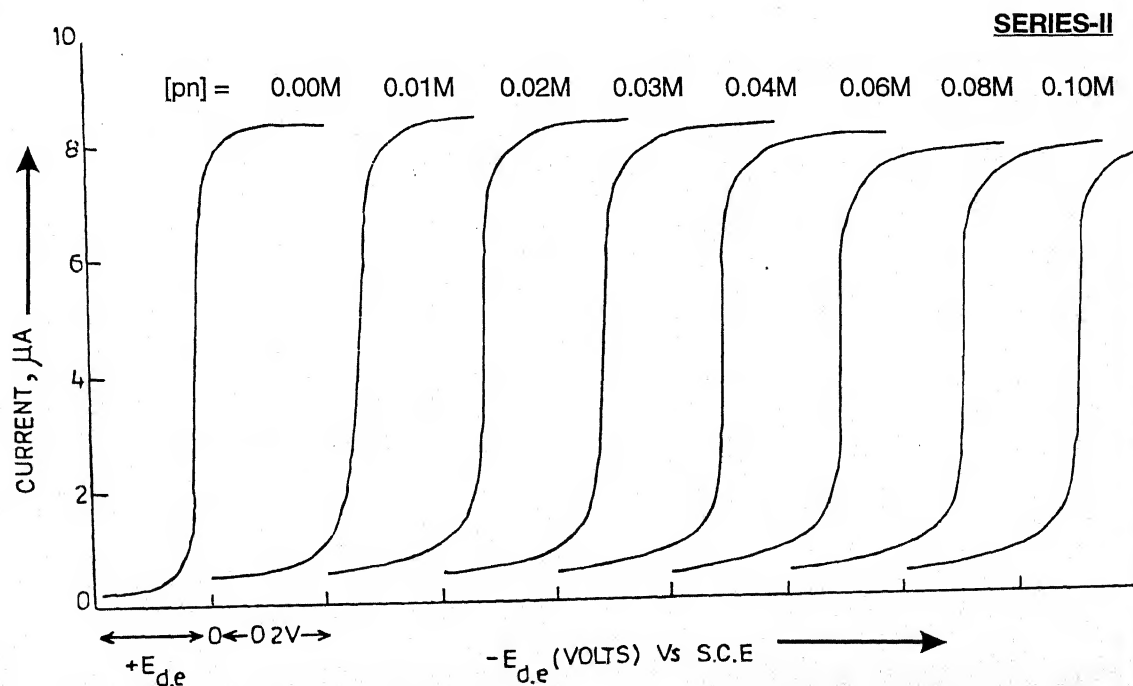
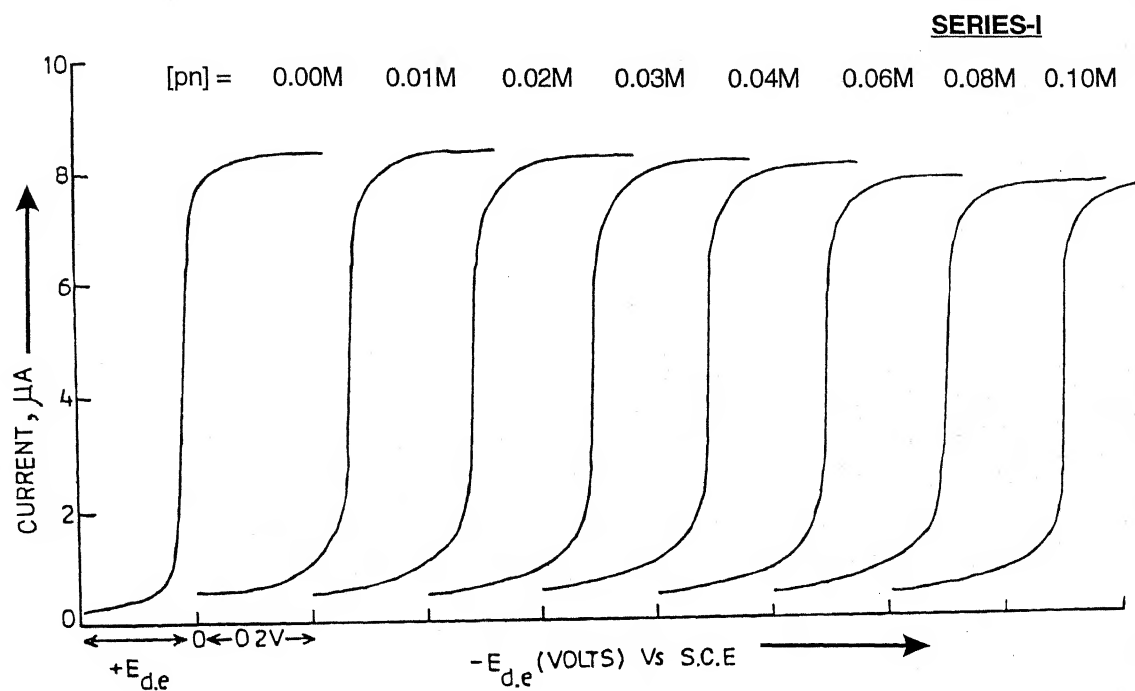
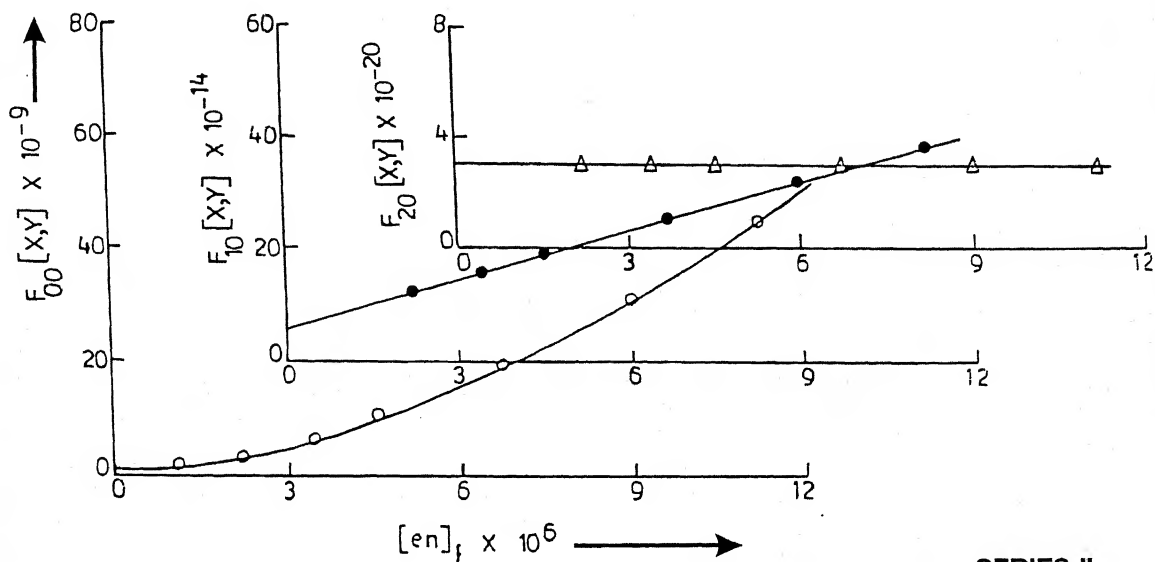


FIG. 5.24 POLAROGRAPHIC WAVES OF Cu (II) - PROPYLENEDIAMINE - L - ISOLEUCINE SYSTEM

SERIES-I



SERIES-II

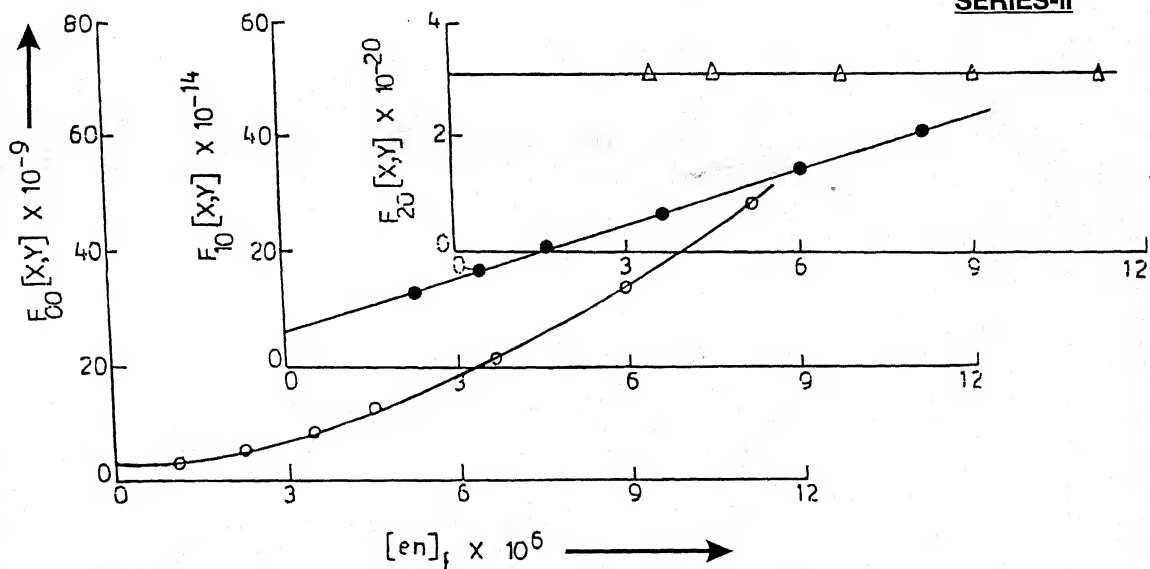


FIG. 5.25 PLOT OF $F_i[X,Y]$ FUNCTIONS FOR Cu(II) - ETHYLENEDIAMINE GLYCINE SYSTEM

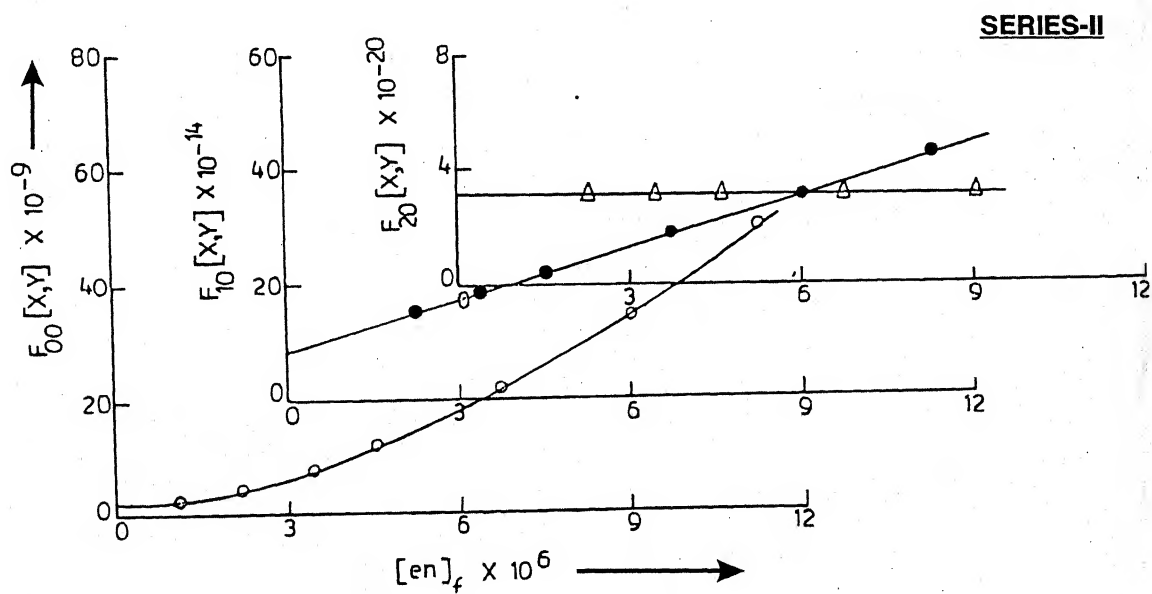
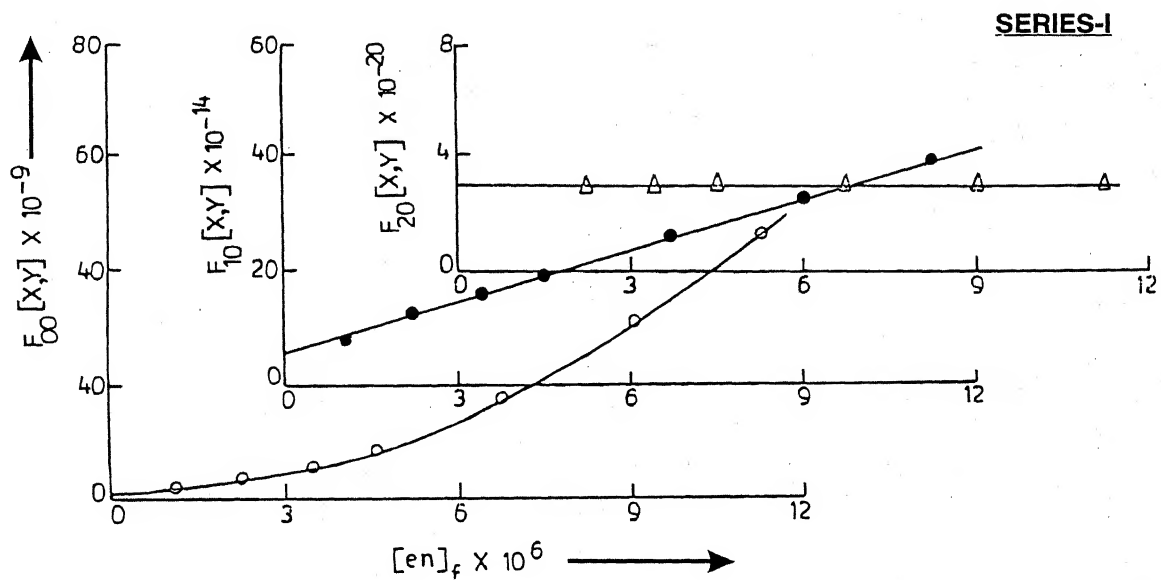
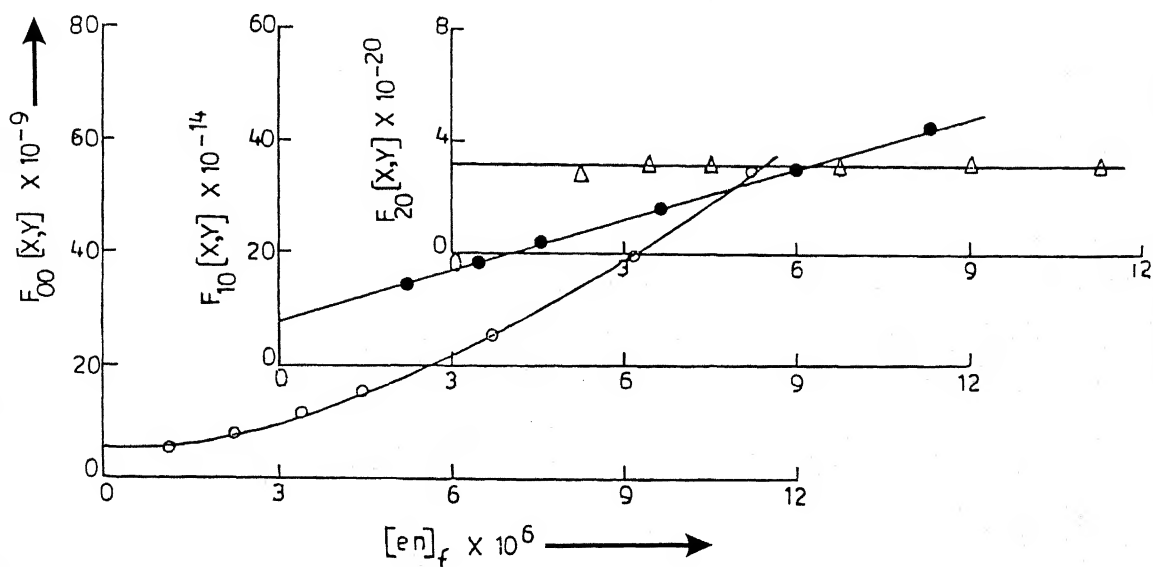


FIG. 5.26 PLOT OF $F_i[X,Y]$ FUNCTIONS FOR Cu (II) - ETHYLENEDIAMINE - DL - ALANINE SYSTEM

SERIES-I



SERIES-II

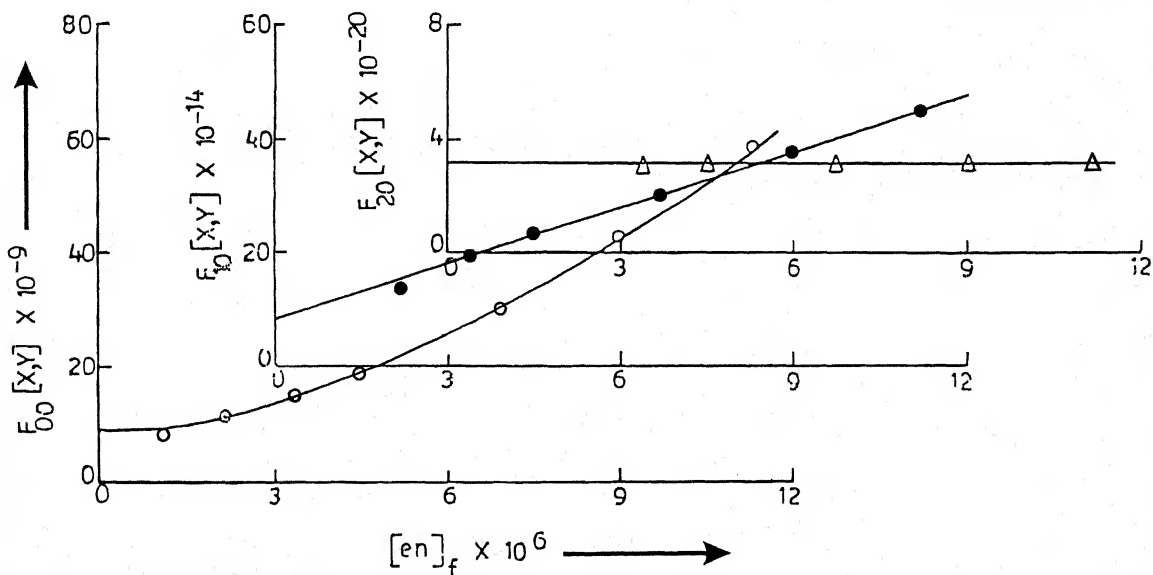
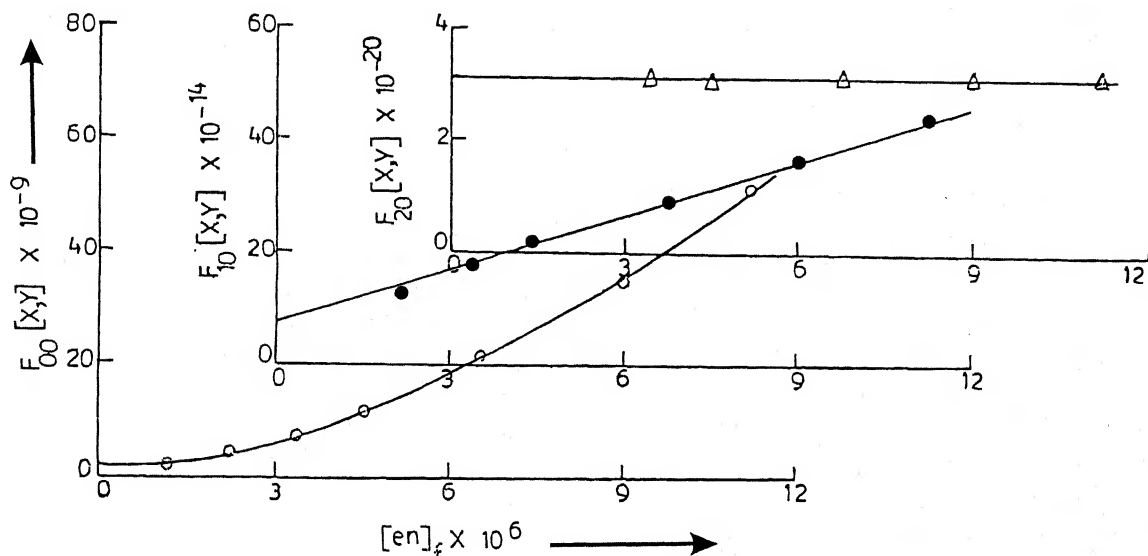


FIG. 5.27 PLOT OF $F_{ij}[X,Y]$ FUNCTIONS FOR Cu (II) - ETHYLENEDIAMINE - DL - VALINE SYSTEM

SERIES-I



SERIES-II

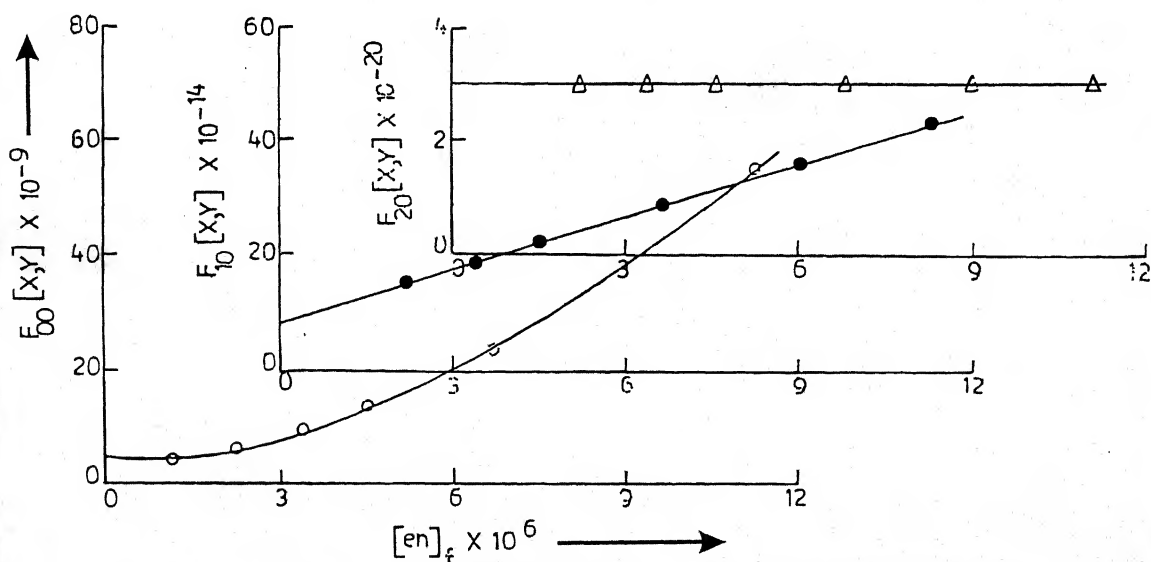


FIG. 5.28 PLOT OF $F_i[X,Y]$ FUNCTIONS FOR Cu (II) - ETHYLENEDIAMINE - L - ISOLEUCINE SYSTEM

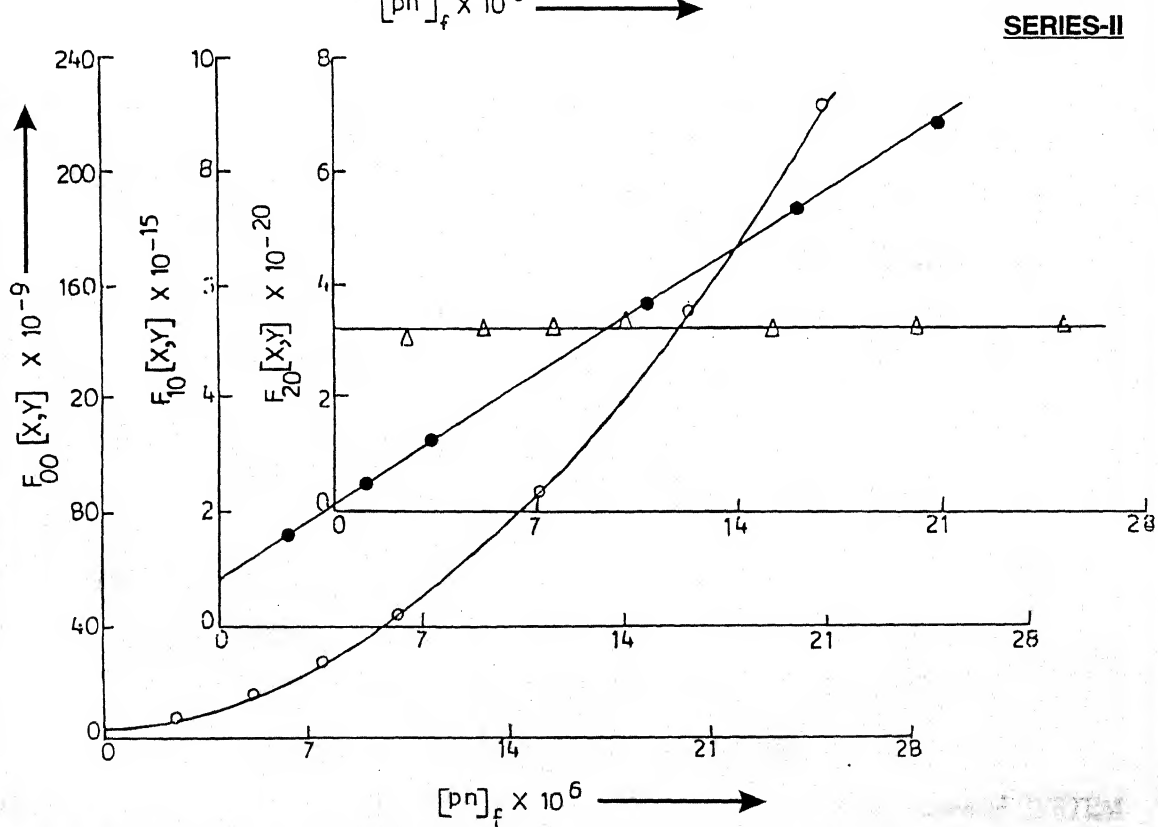
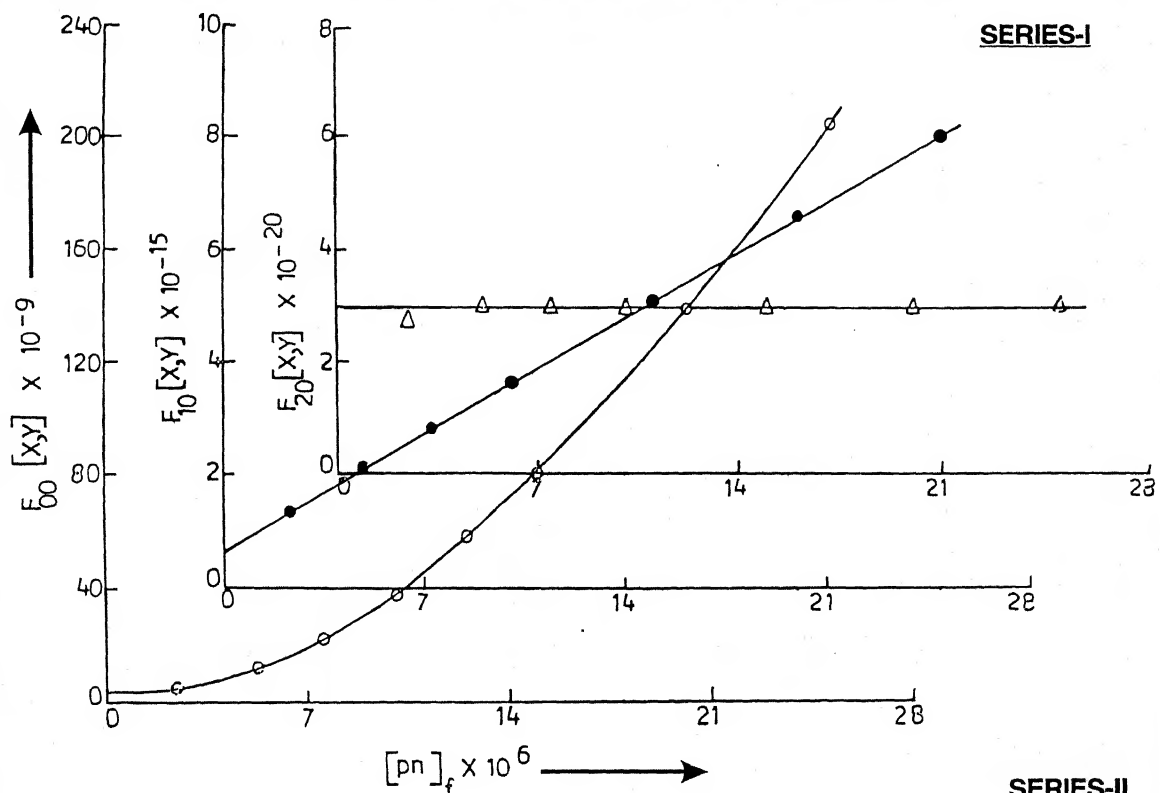


FIG. 5.29 PLOT OF $F_i [X,Y]$ FUNCTIONS FOR Cu (II) - PROPYLENEDIAMINE GLYCINE SYSTEM

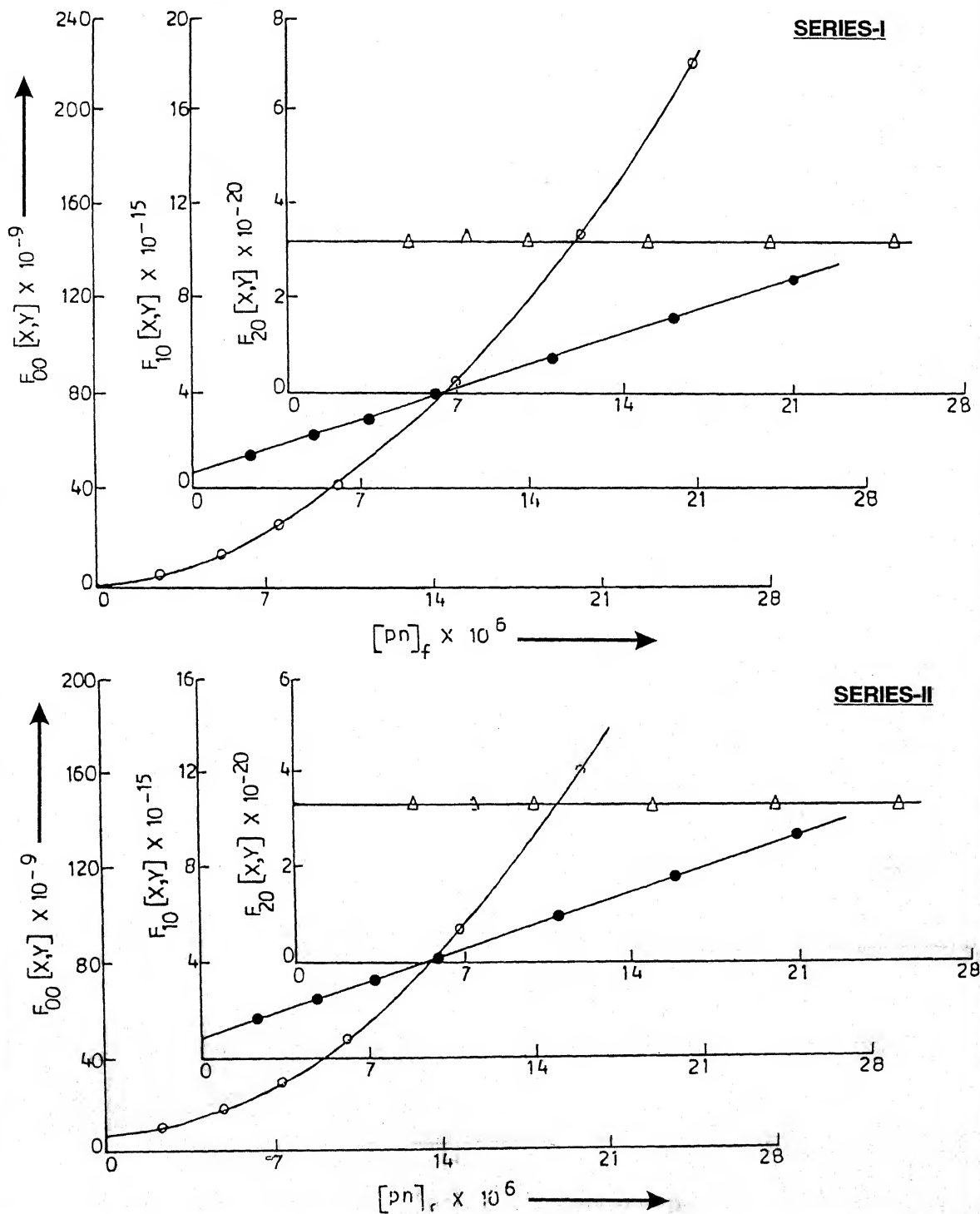


FIG. 5.30 PLOT OF $F_i [X,Y]$ FUNCTION FOR Cu (II) - PROPYLENEDIAMINE - DL - ALANINE SYSTEM

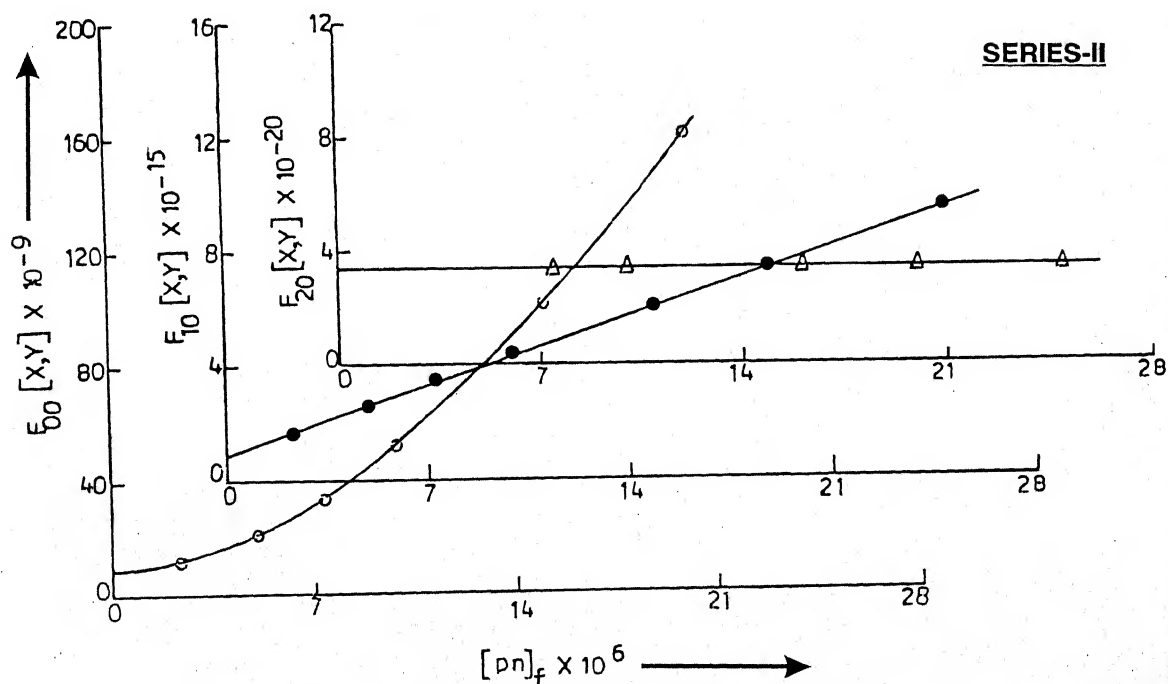
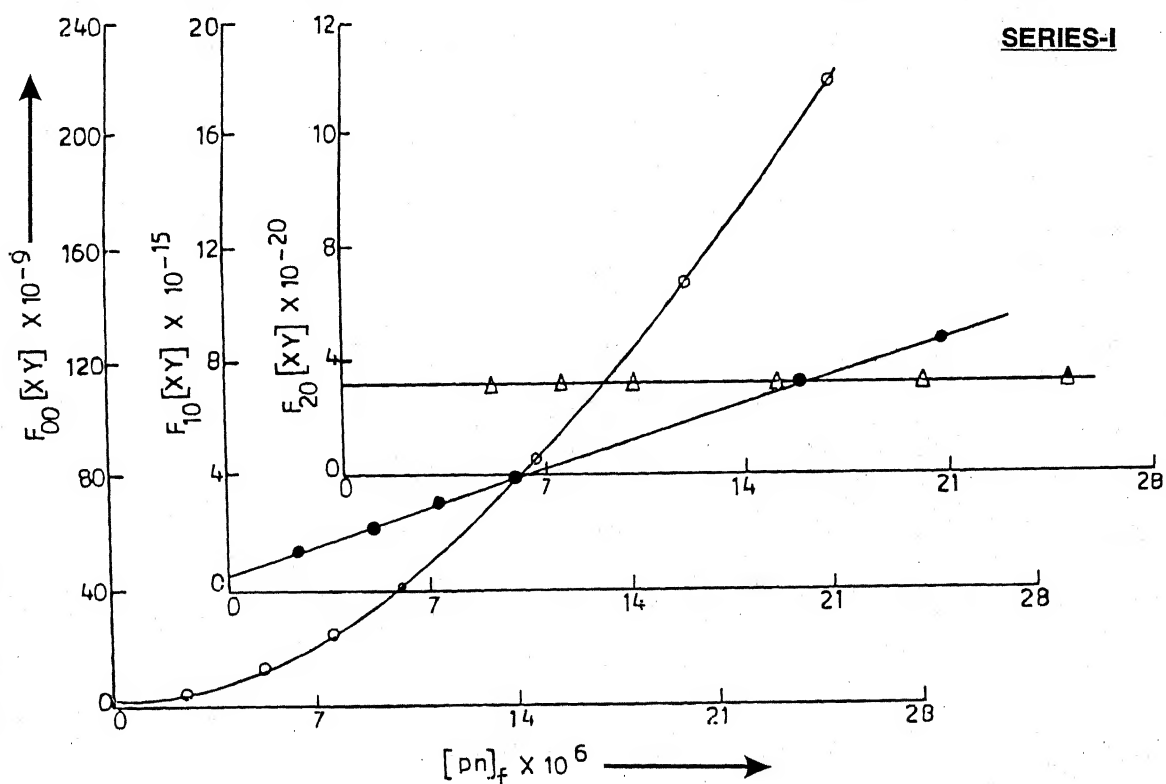


FIG. 5.31 PLOT OF $F_i [X,Y]$ FUNCTION FOR Cu (II) - PROPYLENEDIAMINE - DL - VALINE SYSTEM

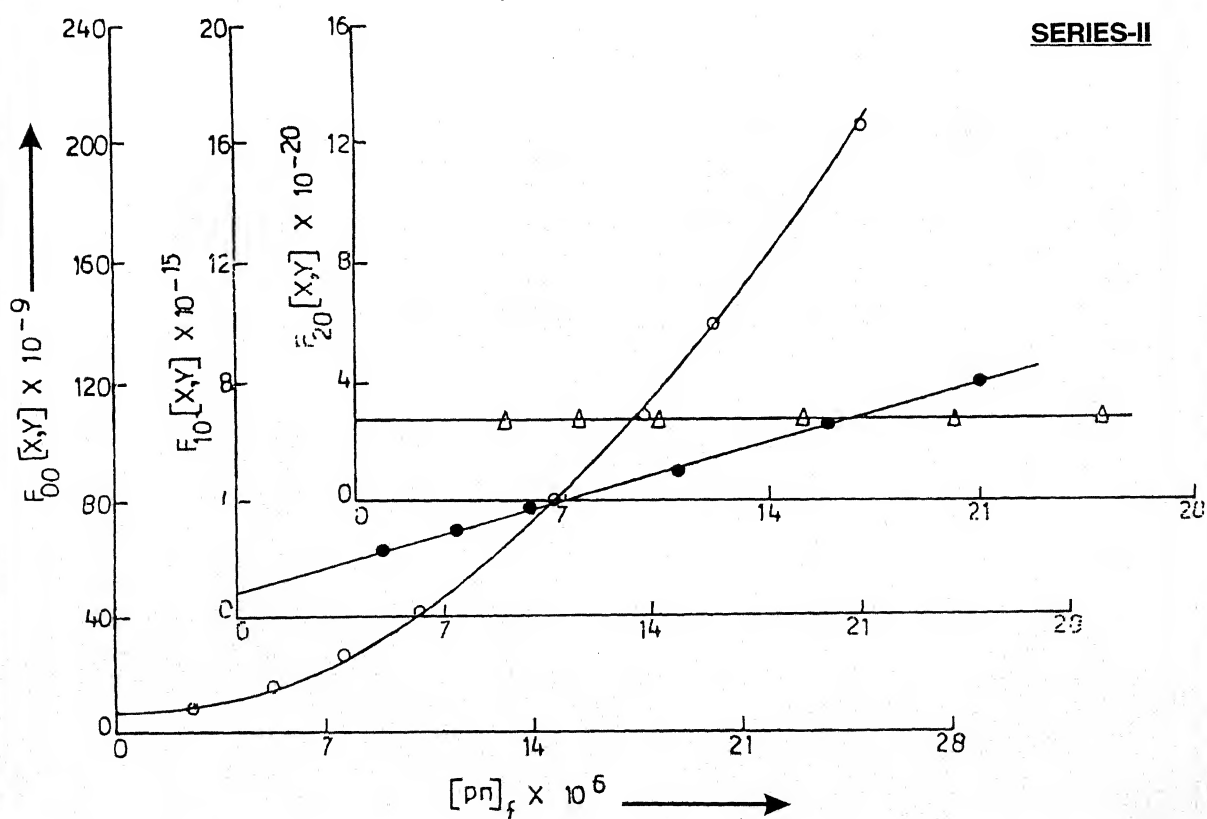
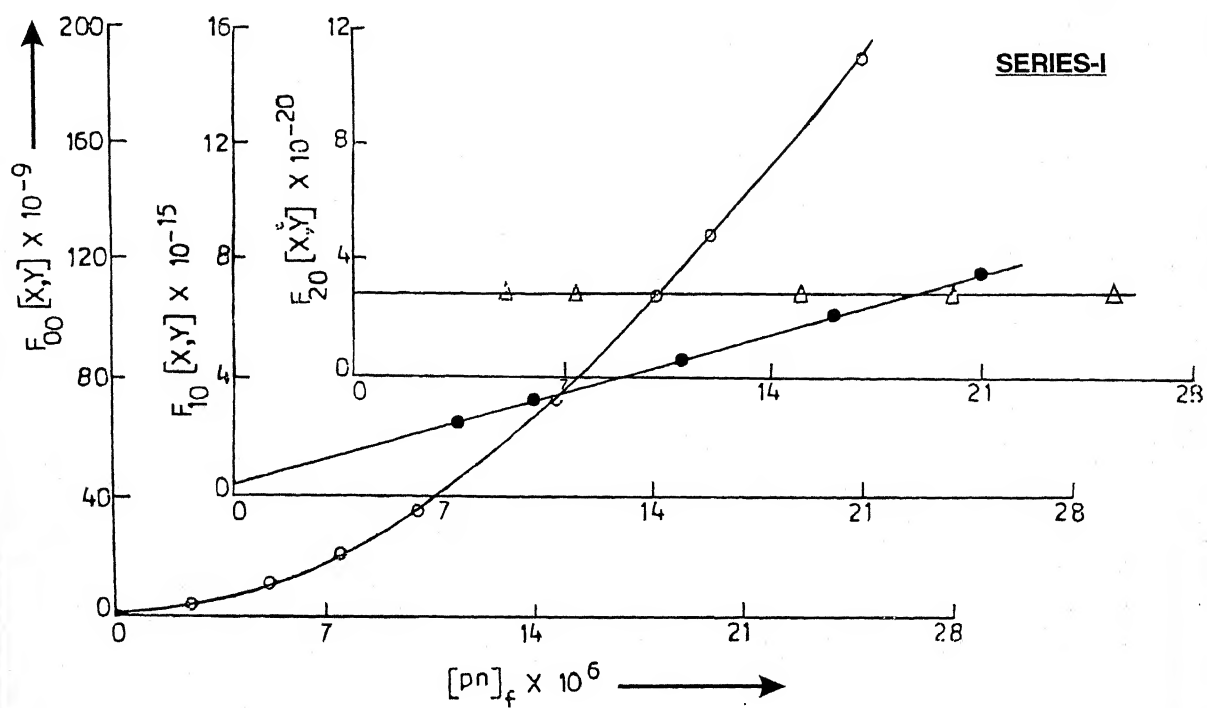


FIG. 5.32 PLOT OF $F_i [X,Y]$ FUNCTIONS FOR Cu (II) - PROPYLENEDIAMINE - L - ISOLEUCINE SYSTEM

TABLE 5.01

POLAROGRAPHIC FUNCTIONS OF THE SIMPLE Cu (II) - ETHYLENEDIAMINE SYSTEM

$[\text{en}]_t$	$[\text{en}]_f$	$\log \frac{I_M}{I_C}$	$\Delta E_{1/2}$	Slope	$F_0 [x]$	$F_1 [x]$	$F_2 [x]$
M	$\times 10^6$ M		V	mV	$\times 10^{-8}$	$\times 10^{-14}$	$\times 10^{-20}$
0.01	1.1	—	—	29	6.42	5.77	—
0.02	2.2	.0083	0.013	29	18.04	8.05	2.90
0.03	3.4	.0225	0.022	30	37.59	11.19	2.84
0.04	4.5	.0225	0.029	30	64.88	14.48	2.90
0.06	6.7	.0283	0.039	31	143.34	21.29	2.92
0.08	9.0	.0354	0.046	31	251.43	28.03	2.94
0.10	11.2	.0524	0.051	31	386.05	34.44	2.93

$[\text{en}]_t$ = Total (analytical) concentration of ethylenediamine (en)

$[\text{en}]_f$ = Free ligand concentration of ethylenediamine (en)

$[\text{Cu}^{2+}] = 1.0 \times 10^{-3} \text{ M}$, $\mu = 1.0$ (NaNO_3), pH = 6.60, Temp. = $25 \pm 0.1^\circ\text{C}$

TABLE 5.02

POLAROGRAPHIC FUNCTIONS OF THE SIMPLE Cu (II) - PROPYLENEDIAMINE SYSTEM

$[pn]_t$	$[pn]_f$	$\log \frac{I_M}{I_C}$	$\Delta E_{1/2}$	Slope	$F_0 [x]$	$F_1 [x]$	$F_2 [x]$
M	$\times 10^6$ M		V	mV	$\times 10^{-9}$	$\times 10^{-16}$	$\times 10^{-20}$
0.01	2.5	—	—	29	3.57	—	—
0.02	5.0	.0055	0.009	29	7.27	14.49	2.10
0.03	7.5	.0111	0.018	29	14.89	19.78	2.10
0.04	10.0	.0156	0.025	30	25.97	25.86	2.17
0.06	15.1	.0236	0.034	30	53.34	35.42	2.10
0.08	20.1	.0301	0.041	31	93.42	46.49	2.11
0.10	25.1	.0426	0.046	31	141.99	56.55	2.10

$[pn]_t$ = Total (analytical) concentration of propylenediamine (pn)

$[pn]_f$ = Free ligand concentration of propylenediamine (pn)

$[Cu^{2+}] = 1.0 \times 10^{-3}$ M, $\mu = 1.0$ (NaNO₃), pH = 6.60, Temp. = $25 \pm 0.1^\circ\text{C}$

TABLE 5.03

POLAROGRAPHIC FUNCTIONS OF THE SIMPLE Cu (II) - GLYCINE SYSTEM

[gly]	[gly ⁻] _f	$\log \frac{I_M}{I_C}$	$\Delta E_{1/2}$	Slope	F ₀ [x]	F ₁ [x]	F ₂ [x]
M	X 10 ⁵ M		V	mV	X 10 ⁻⁸	X 10 ⁻¹³	X 10 ⁻¹⁵
0.1	6.6	—	—	29	1.27	19.29	—
0.2	13.2	.0068	0.011	30	3.05	23.09	3.10
0.3	19.8	.0079	0.018	30	5.27	26.64	3.85
0.4	26.4	.0229	0.022	31	7.46	28.23	3.50
0.5	33.0	.0229	0.026	31	10.18	30.85	3.55
0.6	39.6	.0283	0.029	31	13.02	32.88	3.50

[gly] = Total (analytical) concentration of glycine (gly)

[gly⁻] = Glycinate ion concentration.

[Cu²⁺] = 1.0 X 10⁻³ M, μ = 1.0 (NaNO₃), pH = 6.60, Temp. = 25 ± 0.1°C

TABLE 5.04

POLAROGRAPHIC FUNCTIONS OF THE SIMPLE Cu^{2+} (II) - DL - ALANINE SYSTEM

[ala] M	[ala ⁻] X 10 ⁵ M	$\log \frac{I_M}{I_C}$	$\Delta E_{1/2}$ V	Slope mV	F ₀ [x] X 10 ⁻⁸	F ₁ [x] X 10 ⁻¹³	F ₂ [x] X 10 ⁻¹⁵
0.1	5.4	—	—	29	1.09	20.29	—
0.2	10.7	.0073	0.009	29	2.23	20.79	2.60
0.3	16.1	.0124	0.015	30	3.60	22.38	2.72
0.4	21.5	.0193	0.019	30	5.01	23.33	2.50
0.5	26.8	.0193	0.023	31	6.83	25.46	2.70
0.6	32.2	.0270	0.026	31	8.78	27.28	2.75

[ala] = Total (analytical) concentration of alanine (ala)

[ala⁻] = Alaninate ion concentration.

[Cu²⁺] = 1.0 X 10⁻³ M, μ = 1.0 (NaNO₃), pH = 6.60, Temp. = 25 ± 0.1°C

TABLE 5.05

POLAROGRAPHIC FUNCTIONS OF THE SIMPLE Cu (II) - DL - VALINE SYSTEM

[val] M	[val ⁻] X 10 ⁵ M	log $\frac{I_M}{I_c}$	$\Delta E_{1/2}$ V	Slope mV
0.1	7.6	—	—	29
0.2	15.2	.0028	0.012	30
0.3	22.7	.0056	0.022	30
0.4	30.3	.0096	0.026	30
0.5	37.9	.0113	0.030	31
0.6	45.5	.0119	0.036	31

[val] = Total (analytical) concentration of valine (val)

[val⁻] = Valinate ion concentration.

[Cu²⁺] = 1.0 X 10⁻³ M, μ = 1.0 (NaNO₃), pH = 6.60, Temp. = 25 ± 0.1°C

TABLE 5.06

POLAROGRAPHIC FUNCTIONS OF THE SIMPLE Cu (II) - L - ISOLEUCINE SYSTEM

[isolc] M	[Isolc ⁻] X 10 ⁵ M	$\log \frac{I_M}{I_c}$	$\Delta E_{1/2}$ V	Slope mV
0.1	7.1	—	—	29
0.2	14.1	.0051	0.016	29
0.3	21.2	.0103	0.022	30
0.4	28.3	.0138	0.030	30
0.5	35.4	.0209	0.034	31
0.6	42.4	.0281	0.040	31

[Isolc] = Total (analytical) concentration of isoleucine (Isolc)

[Isolc⁻] = Isoleucinate ion concentration.

[Cu²⁺] = 1.0 X 10⁻³ M, μ = 1.0 (NaNO₃), pH = 6.60, Temp. = 25 ± 0.1°C

TABLE 5.07

POLAROGRAPHIC FUNCTIONS OF THE MIXED Cu (II) - ETHYLENEDIAMINE**GLYCINE SYSTEM**

$[en]_t$	$[en]_f$	$\log \frac{I_M}{I_C}$	$\Delta E_{1/2}$	Slope	$F_{00} [X,Y]$	$F_{10} [X,Y]$	$F_{20} [X,Y]$
M	$\times 10^6$ M		V	mV	$\times 10^{-9}$	$\times 10^{-14}$	$\times 10^{-20}$
0.01	1.1	—	—	29	2.24	—	—
0.02	2.2	.0022	0.009	29	4.54	11.36	2.61
0.03	3.4	.0044	0.015	30	7.29	15.75	3.04
0.04	4.5	.0044	0.020	30	10.76	19.56	3.13
0.06	6.7	.0028	0.027	30	18.94	25.17	2.97
0.08	9.0	.0197	0.033	31	30.71	32.00	2.98
0.10	11.2	.0208	0.038	31	45.47	38.47	3.00

SERIES I : [gly] = 0.1 M

$[en]_t$	$[en]_f$	$\log \frac{I_M}{I_C}$	$\Delta E_{1/2}$	Slope	$F_{00} [X,Y]$	$F_{10} [X,Y]$	$F_{20} [X,Y]$
M	$\times 10^6$ M		V	mV	$\times 10^{-9}$	$\times 10^{-14}$	$\times 10^{-20}$
0.01	1.1	—	—	29	2.63	—	—
0.02	2.2	.0066	0.010	29	5.81	12.57	2.70
0.03	3.4	.0100	0.015	30	8.65	16.82	3.10
0.04	4.5	.0180	0.019	30	12.04	20.18	3.06
0.06	6.7	.0197	0.026	31	20.85	26.53	3.06
0.08	9.0	.0238	0.032	31	33.59	34.11	3.10
0.10	11.2	.0238	0.037	31	49.61	41.57	3.12

SERIES II : [gly] = 0.2 M

$[Cu^{2+}] = 1.0 \times 10^{-3} M$, $\mu = 1.0$ (NaNO₃), pH = 6.60, Temp. = $25 \pm 0.1^\circ C$

TABLE 5.08

POLAROGRAPHIC FUNCTIONS OF THE MIXED Cu (II) - ETHYLENEDIAMINE**- DL - ALANINE SYSTEM**

$[en]_t$	$[en]_f$	$\log \frac{I_M}{I_c}$	$\Delta E_{1/2}$	Slope	$F_{00} [X,Y]$	$F_{10} [X,Y]$	$F_{20} [X,Y]$
M	$\times 10^6$ M		V	mV	$\times 10^{-9}$	$\times 10^{-14}$	$\times 10^{-20}$
0.01	1.1	—	—	29	1.76	6.84	—
0.02	2.2	.0066	0.009	29	3.61	11.68	2.75
0.03	3.4	.0105	0.016	29	6.39	15.76	3.05
0.04	4.5	.0184	0.021	30	9.40	18.76	3.00
0.06	6.7	.0247	0.029	30	17.68	24.79	2.90
0.08	9.0	.0294	0.036	31	30.91	33.35	3.05
0.10	11.2	.0323	0.041	31	46.20	40.33	3.10

SERIES I : [ala] = 0.1 M

$[en]_t$	$[en]_f$	$\log \frac{I_M}{I_c}$	$\Delta E_{1/2}$	Slope	$F_{00} [X,Y]$	$F_{10} [X,Y]$	$F_{20} [X,Y]$
M	$\times 10^6$ M		V	mV	$\times 10^{-9}$	$\times 10^{-14}$	$\times 10^{-20}$
0.01	1.1	—	—	29	2.43	3.81	—
0.02	2.2	.0050	0.010	29	5.35	14.96	3.10
0.03	3.4	.0089	0.015	30	7.97	17.78	3.00
0.04	4.5	.0157	0.020	30	11.96	22.23	3.17
0.06	6.7	.0220	0.027	31	20.94	28.14	3.00
0.08	9.0	.0267	0.033	31	33.78	35.43	3.15
0.10	11.2	.0296	0.038	31	50.22	43.01	3.12

SERIES II : [ala] = 0.2 M

$[Cu^{2+}] = 1.0 \times 10^{-3} M$, $\mu = 1.0$ (NaNO₃), pH = 6.60, Temp. = $25 \pm 0.1^\circ C$

TABLE 5.09

POLAROGRAPHIC FUNCTIONS OF THE MIXED Cu (II) - ETHYLENEDIAMINE**- DL - VALINE SYSTEM**

$[en]_t$	$[en]_f$	$\log \frac{I_M}{I_c}$	$\Delta E_{1/2}$	Slope	$F_{00} [X,Y]$	$F_{10} [X,Y]$	$F_{20} [X,Y]$
M	$\times 10^6$ M		V	mV	$\times 10^{-9}$	$\times 10^{-14}$	$\times 10^{-20}$
0.01	1.1	—	—	29	4.91	—	—
0.02	2.2	.0039	0.007	29	8.54	13.58	2.71
0.03	3.4	.0045	0.011	30	11.68	18.40	3.24
0.04	4.5	.0198	0.014	30	15.29	21.85	3.20
0.06	6.7	.0291	0.020	30	24.94	28.88	3.20
0.08	9.0	.0291	0.026	31	39.81	37.13	3.30
0.10	11.2	.0327	0.030	31	54.91	43.99	3.25

SERIES I : [val] = 0.1 M

$[en]_t$	$[en]_f$	$\log \frac{I_M}{I_c}$	$\Delta E_{1/2}$	Slope	$F_{00} [X,Y]$	$F_{10} [X,Y]$	$F_{20} [X,Y]$
M	$\times 10^6$ M		V	mV	$\times 10^{-9}$	$\times 10^{-14}$	$\times 10^{-20}$
0.01	1.1	—	—	29	6.32	—	—
0.02	2.2	.0243	0.008	29	11.97	13.28	—
0.03	3.4	.0120	0.011	30	15.31	18.77	3.05
0.04	4.5	.0120	0.014	30	19.34	23.08	3.25
0.06	6.7	.0207	0.019	31	29.14	29.93	3.20
0.08	9.0	.0219	0.024	31	43.15	38.07	3.29
0.10	11.2	.0243	0.028	31	59.26	44.83	3.24

SERIES II : [val] = 0.2 M

$[Cu^{2+}] = 1.0 \times 10^{-3} M$, $\mu = 1.0$ (NaNO₃), pH = 6.60, Temp. = $25 \pm 0.1^\circ C$

TABLE 5.10

POLAROGRAPHIC FUNCTIONS OF THE MIXED Cu (II) - ETHYLENEDIAMINE- L - ISOLEUCINE SYSTEM

$[en]_t$	$[en]_f$	$\log \frac{I_M}{I_c}$	$\Delta E_{1/2}$	Slope	$F_{00} [X,Y]$	$F_{10} [X,Y]$	$F_{20} [X,Y]$
M	$\times 10^6$ M		V	mV	$\times 10^{-9}$	$\times 10^{-14}$	$\times 10^{-20}$
0.01	1.1	—	—	29	2.09	—	—
0.02	2.2	.0050	0.010	29	4.62	11.69	—
0.03	3.4	.0118	0.017	30	8.09	18.15	3.17
0.04	4.5	.0181	0.021	30	11.22	20.58	3.00
0.06	6.7	.0246	0.029	31	21.25	28.60	3.13
0.08	9.0	.0281	0.035	31	34.19	35.89	3.16
0.10	11.2	.0317	0.040	31	50.91	43.63	3.22

SERIES I : [Isolc] = 0.1 M

$[en]_t$	$[en]_f$	$\log \frac{I_M}{I_c}$	$\Delta E_{1/2}$	Slope	$F_{00} [X,Y]$	$F_{10} [X,Y]$	$F_{20} [X,Y]$
M	$\times 10^6$ M		V	mV	$\times 10^{-9}$	$\times 10^{-14}$	$\times 10^{-20}$
0.01	1.1	—	—	29	3.60	—	—
0.02	2.2	.0084	0.009	29	7.39	15.15	3.00
0.03	3.4	.0090	0.013	30	10.13	18.23	2.90
0.04	4.5	.0141	0.017	30	13.99	22.31	3.08
0.06	6.7	.0204	0.023	31	22.66	27.73	2.85
0.08	9.0	.0257	0.029	31	36.62	36.37	3.10
0.10	11.2	.0304	0.034	31	50.57	41.54	2.95

SERIES II : [Isolc] = 0.2 M

$[Cu^{2+}] = 1.0 \times 10^{-3} \text{ M}$, $\mu = 1.0 \text{ (NaNO}_3\text{)}$, pH = 6.60, Temp. = $25 \pm 0.1^\circ\text{C}$

TABLE 5.11

POLAROGRAPHIC FUNCTIONS OF THE MIXED Cu (II) - PROPYLENEDIAMINE**GLYCINE SYSTEM**

$[pn]_t$	$[pn]_f$	$\log \frac{I_M}{I_c}$	$\Delta E_{1/2}$	Slope	$F_{00} [X,Y]$	$F_{10} [X,Y]$	$F_{20} [X,Y]$
M	$\times 10^6$ M		V	mV	$\times 10^{-9}$	$\times 10^{-15}$	$\times 10^{-20}$
0.01	2.5	—	—	29	6.21	1.28	2.70
0.02	5.0	.0050	0.010	29	13.69	2.13	3.04
0.03	7.5	.0095	0.017	30	23.87	2.77	2.90
0.04	10.0	.0169	0.023	30	38.75	3.56	2.94
0.06	15.1	.0250	0.032	30	79.62	5.08	3.00
0.08	20.1	.0285	0.039	31	138.50	6.74	3.05
0.10	25.1	.0321	0.044	31	206.21	8.09	3.00

SERIES I : [gly] = 0.1 M

$[pn]_t$	$[pn]_f$	$\log \frac{I_M}{I_c}$	$\Delta E_{1/2}$	Slope	$F_{00} [X,Y]$	$F_{10} [X,Y]$	$F_{20} [X,Y]$
M	$\times 10^6$ M		V	mV	$\times 10^{-9}$	$\times 10^{-15}$	$\times 10^{-20}$
0.01	2.5	—	—	29	7.90	1.55	3.00
0.02	5.0	.0039	0.009	29	16.08	2.41	3.20
0.03	7.5	.0107	0.016	29	28.18	3.21	3.20
0.04	10.0	.0147	0.022	30	45.40	4.12	3.31
0.06	15.1	.0229	0.030	30	86.31	5.46	3.12
0.08	20.1	.0276	0.037	31	150.56	7.29	3.23
0.10	25.1	.0300	0.042	31	223.54	8.74	3.20

SERIES II : [gly] = 0.2 M

$[Cu^{2+}] = 1.0 \times 10^{-3} M$, $\mu = 1.0$ (NaNO₃), pH = 6.60, Temp. = $25 \pm 0.1^\circ C$

TABLE 5.12

POLAROGRAPHIC FUNCTIONS OF THE MIXED Cu (II) - PROPYLENEDIAMINE- DL - ALANINE SYSTEM

$[pn]_t$	$[pn]_f$	$\log \frac{I_M}{I_c}$	$\Delta E_{1/2}$	Slope	$F_{00} [X,Y]$	$F_{10} [X,Y]$	$F_{20} [X,Y]$
M	$\times 10^6$ M		V	mV	$\times 10^{-9}$	$\times 10^{-15}$	$\times 10^{-20}$
0.01	2.5	—	—	29	5.71	1.28	2.70
0.02	5.0	.0044	0.010	29	13.60	2.21	3.20
0.03	7.5	.0105	0.018	30	25.73	3.08	3.30
0.04	10.0	.0151	0.024	30	41.51	3.88	3.27
0.06	15.1	.0225	0.033	31	85.15	5.48	3.24
0.08	20.1	.0249	0.040	31	147.71	7.23	3.29
0.10	25.1	.0325	0.045	31	22.99	8.74	3.24

SERIES I : $[ala] = 0.1 \text{ M}$

$[pn]_t$	$[pn]_f$	$\log \frac{I_M}{I_c}$	$\Delta E_{1/2}$	Slope	$F_{00} [X,Y]$	$F_{10} [X,Y]$	$F_{20} [X,Y]$
M	$\times 10^6$ M		V	mV	$\times 10^{-9}$	$\times 10^{-15}$	$\times 10^{-20}$
0.01	2.5	—	—	29	9.92	1.56	—
0.02	5.0	.0062	0.008	29	18.76	2.54	3.30
0.03	7.5	.0141	0.014	30	30.51	3.25	3.12
0.04	10.0	.0141	0.020	30	48.70	4.25	3.35
0.06	15.1	.0222	0.028	31	92.54	5.75	3.21
0.08	20.1	.0222	0.035	31	159.68	7.65	3.35
0.10	25.1	.0257	0.040	31	237.74	9.23	3.31

SERIES II : $[ala] = 0.2 \text{ M}$

$[Cu^{2+}] = 1.0 \times 10^{-3} \text{ M}$, $\mu = 1.0 \text{ (NaNO}_3\text{)}$, pH = 6.60, Temp. = $25 \pm 0.1^\circ\text{C}$

TABLE 5.13

POLAROGRAPHIC FUNCTIONS OF THE MIXED Cu (II) - PROPYLENEDIAMINE- DL - VALINE SYSTEM

$[pn]_t$	$[pn]_f$	$\log \frac{I_M}{I_C}$	$\Delta E_{1/2}$	Slope	$F_{00} [X,Y]$	$F_{10} [X,Y]$	$F_{20} [X,Y]$
M	$\times 10^6$ M		V	mV	$\times 10^{-9}$	$\times 10^{-15}$	$\times 10^{-20}$
0.01	2.5	—	—	29	6.19	1.27	—
0.02	5.0	.0061	0.010	29	13.70	2.13	3.05
0.03	7.5	.0140	0.018	29	26.03	3.05	3.26
0.04	10.0	.0140	0.024	30	41.56	3.84	3.22
0.06	15.1	.0192	0.033	30	84.81	5.43	3.20
0.08	20.1	.0244	0.040	31	147.71	7.20	3.28
0.10	25.1	.0256	0.045	31	219.30	8.61	3.20

SERIES I : $[val] = 0.1 \text{ M}$

$[pn]_t$	$[pn]_f$	$\log \frac{I_M}{I_C}$	$\Delta E_{1/2}$	Slope	$F_{00} [X,Y]$	$F_{10} [X,Y]$	$F_{20} [X,Y]$
M	$\times 10^6$ M		V	mV	$\times 10^{-9}$	$\times 10^{-15}$	$\times 10^{-20}$
0.01	2.5	—	—	29	12.50	1.39	—
0.02	5.0	.0045	0.007	29	21.79	2.55	3.30
0.03	7.5	.0095	0.013	30	35.19	3.48	3.42
0.04	10.0	.0095	0.018	30	51.97	4.28	3.35
0.06	15.1	.0163	0.026	31	98.48	5.94	3.34
0.08	20.1	.0303	0.032	31	162.31	7.63	3.35
0.10	25.1	.0303	0.037	31	239.66	9.19	3.30

SERIES II : $[val] = 0.2 \text{ M}$

$[Cu^{2+}] = 1.0 \times 10^{-3} \text{ M}$, $\mu = 1.0$ ($NaNO_3$), $pH = 6.60$, $Temp. = 25 \pm 0.1^\circ C$

TABLE 5.14

POLAROGRAPHIC FUNCTIONS OF THE MIXED Cu (II) - PROPYLENEDIAMINE**- L - ISOLEUCINE SYSTEM**

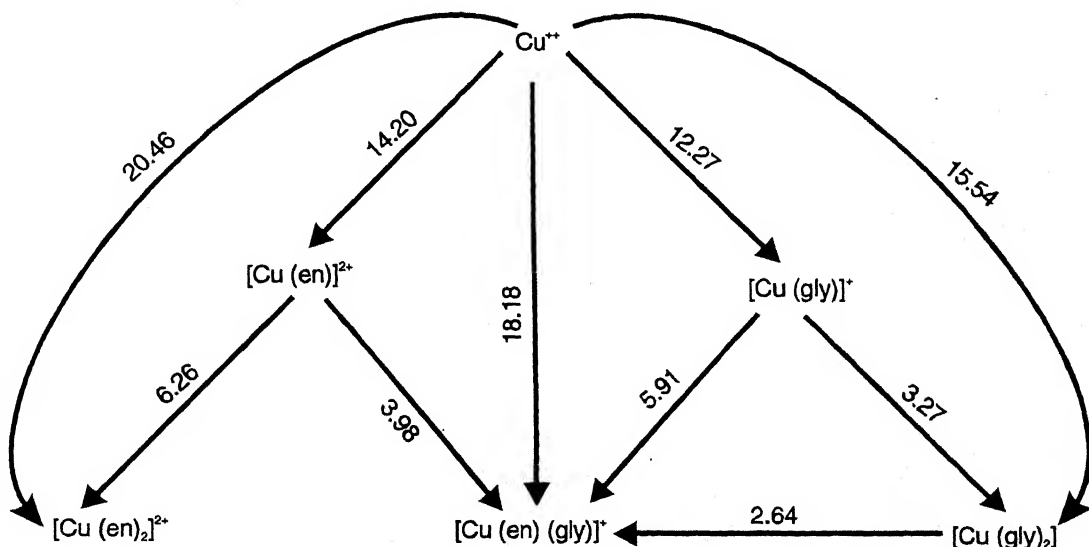
$[pn]_t$	$[pn]_f$	$\log \frac{I_M}{I_c}$	$\Delta E_{1/2}$	Slope	$F_{00} [X,Y]$	$F_{10} [X,Y]$	$F_{20} [X,Y]$
M	$\times 10^6$ M		V	mV	$\times 10^{-9}$	$\times 10^{-15}$	$\times 10^{-20}$
0.01	2.5	—	—	29	5.28	—	—
0.02	5.0	.0044	0.011	29	12.56	1.90	2.81
0.03	7.5	.0089	0.018	30	21.91	2.51	2.67
0.04	10.0	.0168	0.024	30	35.61	3.25	2.73
0.06	15.1	.0249	0.033	31	73.16	4.65	2.80
0.08	20.1	.0296	0.040	31	127.59	6.20	2.83
0.10	25.1	.0355	0.045	31	191.01	7.49	2.80

SERIES I : [Isolc] = 0.1 M

$[pn]_t$	$[pn]_f$	$\log \frac{I_M}{I_c}$	$\Delta E_{1/2}$	Slope	$F_{00} [X,Y]$	$F_{10} [X,Y]$	$F_{20} [X,Y]$
M	$\times 10^6$ M		V	mV	$\times 10^{-9}$	$\times 10^{-15}$	$\times 10^{-20}$
0.01	2.5	—	—	29	7.22	—	—
0.02	5.0	.0050	0.011	29	17.23	2.24	2.86
0.03	7.5	.0123	0.017	29	27.96	2.92	2.81
0.04	10.0	.0203	0.022	30	42.06	3.59	2.78
0.06	15.1	.0249	0.032	30	79.29	4.87	2.70
0.08	20.1	.0296	0.037	31	138.31	6.59	2.88
0.10	25.1	.0356	0.042	31	207.06	8.01	2.87

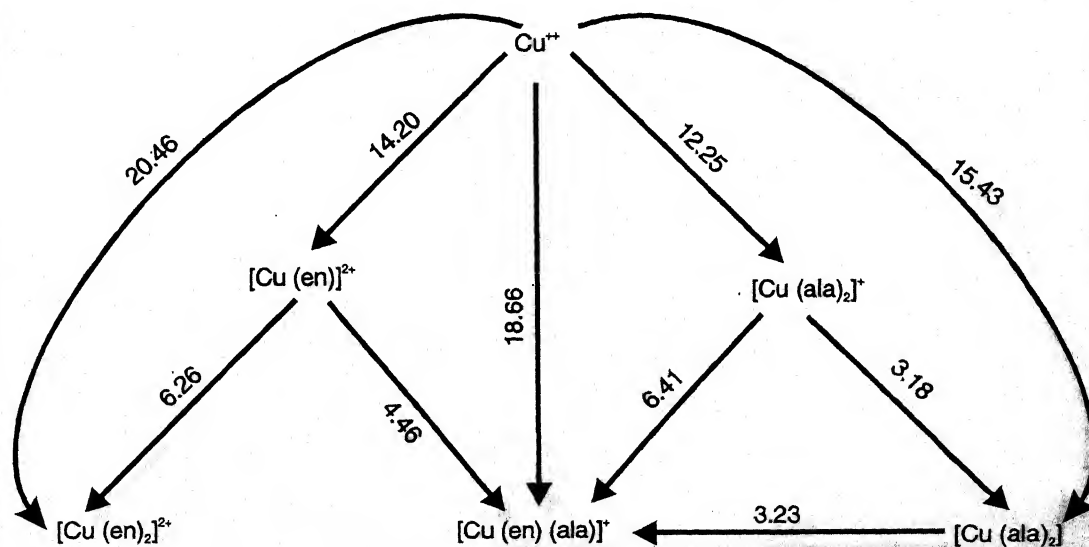
SERIES II : [Isolc] = 0.2 M

$[Cu^{2+}] = 1.0 \times 10^{-3} M$, $\mu = 1.0$ (NaNO₃), pH = 6.60, Temp. = $25 \pm 0.1^\circ C$



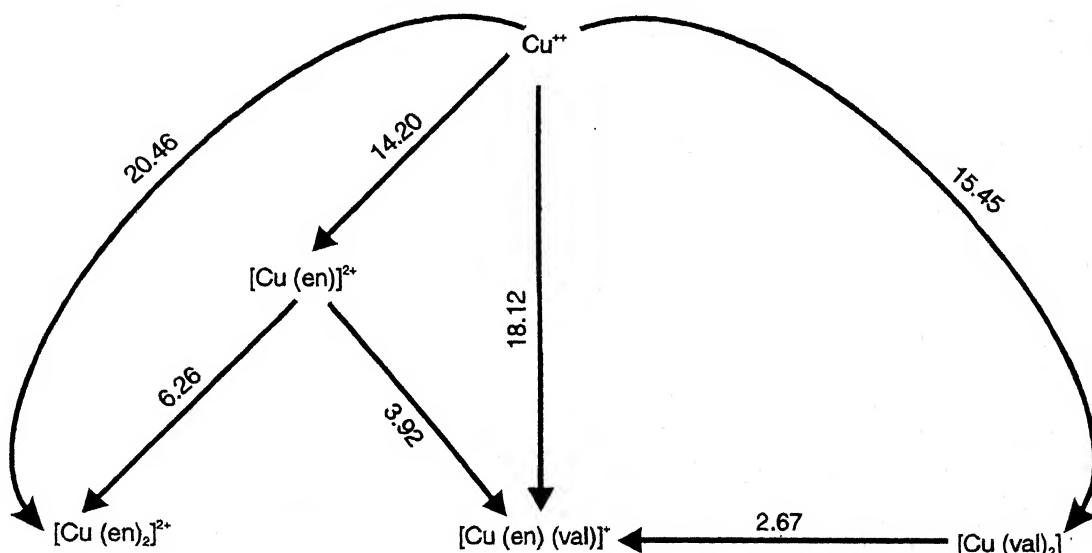
FLWSHEET DIAGRAM - 5.01

COPPER - ETHYLENEDIAMINE - GLYCINE SYSTEM



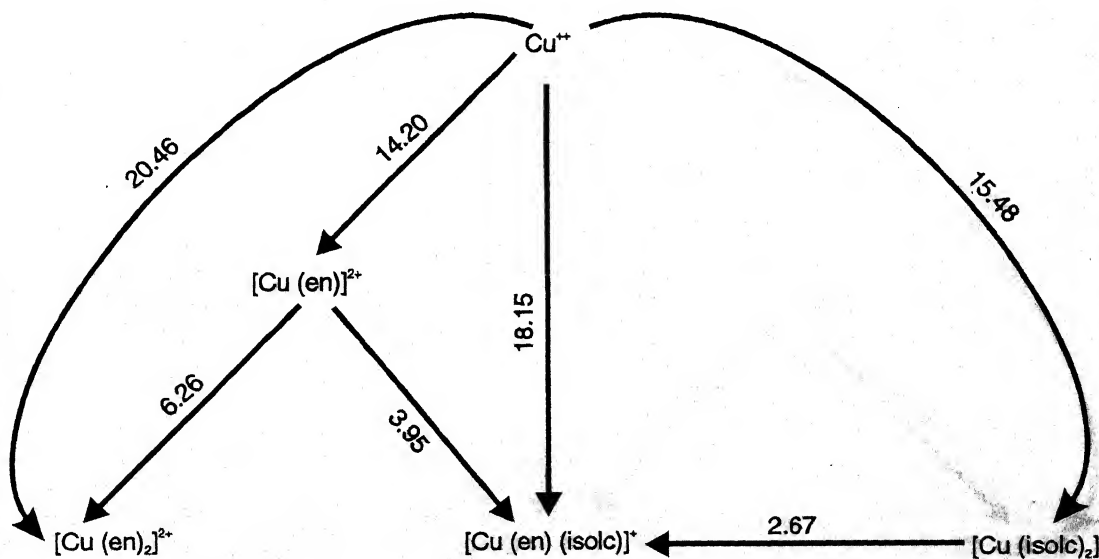
FLWSHEET DIAGRAM - 5.02

COPPER - ETHYLENEDIAMINE - ALANINE SYSTEM



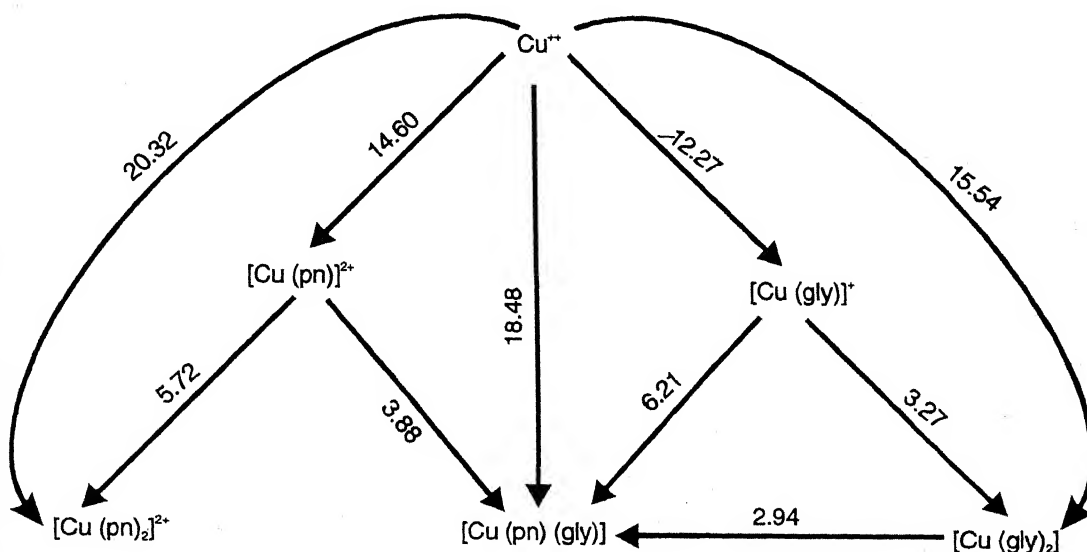
FLWSHEET DIAGRAM - 5.03

COPPER - ETHYLENEDIAMINE - VALINE SYSTEM



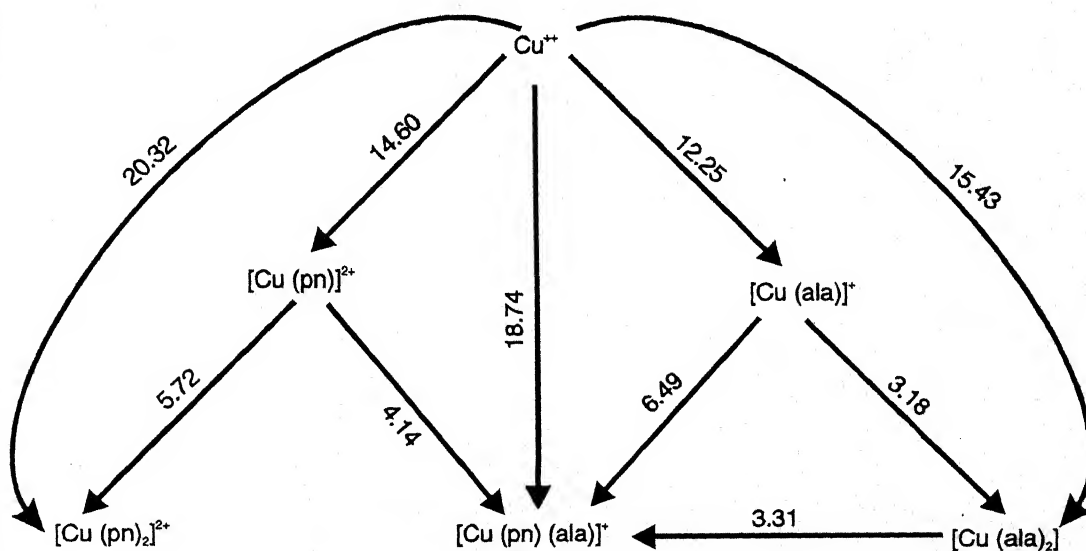
FLWSHEET DIAGRAM - 5.04

COPPER - ETHYLENEDIAMINE - ISOLEUCINE SYSTEM



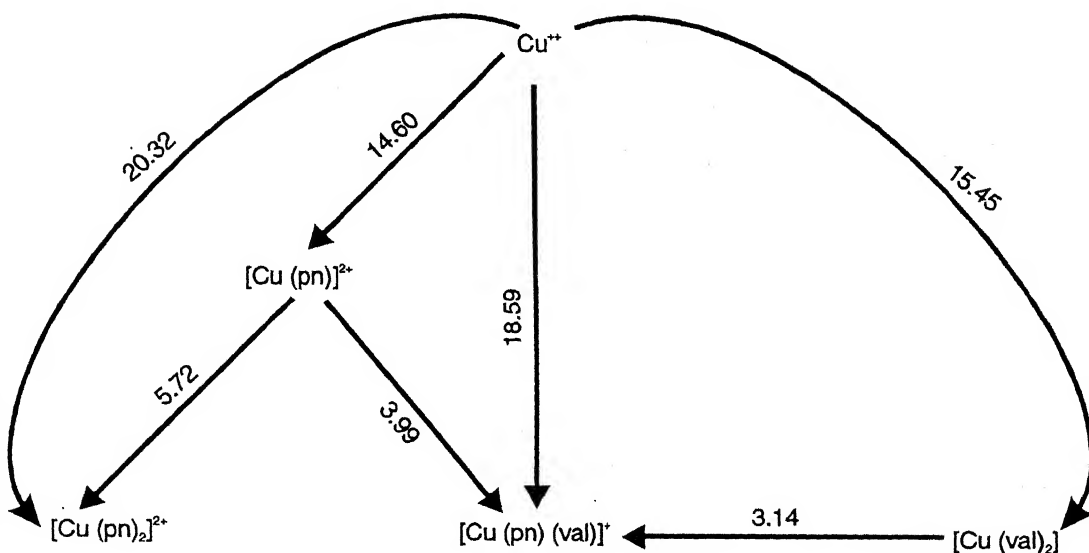
FLWSHEET DIAGRAM - 5.05

COPPER - PROPYLENEDIAMINE - GLYCINE SYSTEM



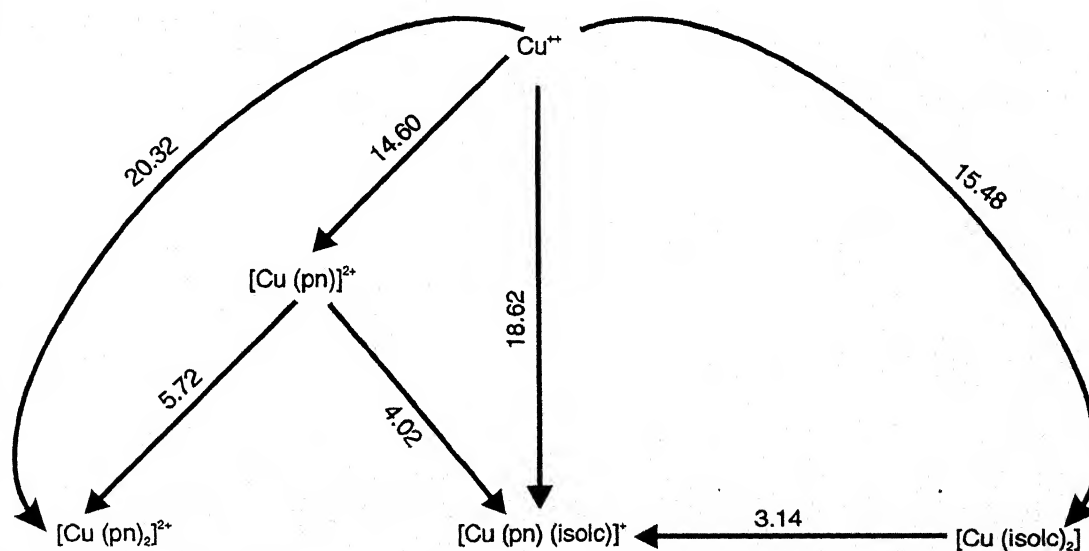
FLWSHEET DIAGRAM - 5.06

COPPER - PROPYLENEDIAMINE - ALANINE SYSTEM



FLWSHEET DIAGRAM - 5.07

COPPER - PROPYLENEDIAMINE - VALINE SYSTEM



FLWSHEET DIAGRAM - 5.08

COPPER - PROPYLENEDIAMINE - ISOLEUCINE SYSTEM

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